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ERRATA

Page.	Line.				
103	3	*For*	Amaresh Chandra Ray	*read*	Amaresh Chandra Roy
285	2	,,	*p*-Amino-	,,	*p*-Aminophenyl
387	12*	,,	$Na_2HPO_4 - H_2O$	,,	$Na_2HPO_4 - H_2O_2$
419	6*	,,	$C_6H_{13}O_6$	,,	$C_{16}H_{13}O_6$
422	15*	,,	*Monobenzyl*	,,	*Monobenzoyl*
435	12*	,,	*Sodium Salt*	,,	*Potassium Salt*
436	17	,,	07	,,	70
439	14	,,	*o*-nitrophenyl	,,	1-*o*-nitrophenyl
455	16*	,,	HS	,,	H_2S
456	7	,,	C_3HS_2	,,	$C_3H_6S_2$
661	5	,,	Tarinikanta	,,	Taranikanta
697	6	,,	Rai-choudhury	,,	Rai-chaudhuri
673	1	,,	γ	,,	ν
674	5	,,	γ	,,	ν.

* From bottom.

Effect of Hemolytic Substances on Red Blood Corpuscles and the Mechanism of Hemolysis.

By K. C. Sen and S. K. Basu.

A large number of workers have studied the hemolysis of red blood corpuscles by different substances (see Hober, *Physikalische Chemie der Zelle und Gewebe*, 1924, p. 499) but as yet no clear explanation exists as to the mechanism of the change in the permeability of the stroma or the corpuscle membrane under the influence of different hemolytes. That a single explanation may not cover all cases is evident from the fact that simply pure water will hemolyse the corpuscles which is entirely due to the absorption of water owing to a difference in the osmotic pressure inside and outside the cell membrane. The membrane is thus ruptured owing to a swelling of the whole cell. While conducting some experiments on the hemolysis of red blood corpuscles by hemolytes, the attention of the authors was drawn to the problem from a different point of view, namely, what effect each individual constituent of the cell has on the properties of the other constituents. Consequently the stability of hemoglobin, lecithin, cholesterol and albumin, which are known to be the chief constituents of the cells, in presence of each other has been investigated, and in this paper a preliminary account of these researches is given.

Experimental.

The hemoglobin sol was prepared by digesting 5 grams of Merck's pure hemoglobin in about 400 c.c. of water for an hour and then filtered. The filtrate was then made up to 500 c.c. The cholesterol suspension was prepared by dissolving about 0·5 gram of the substance (Kahlbaum) in alcohol and then pouring into 500 c.c. of water. The suspension obtained was then filtered. The lecithin sol was prepared by allowing 10 grams of Merck's pure lecithin (nach ova) to imbibe some water for 24 hours, and then emulsifying in 500 c.c. of water. The egg albumin was a crystalline variety obtained from Kahlbaum and was dissolved in water and used without any further

dialysis. Of the different hemolytic agents, saponin was obtained from British Drug Houses, Ltd., sodium taurocholate and glycocholate from Merck and potassium oleate from Kahlbaum. The taurocholate and glycocholate were prepared only a few hours before they were used, as these salt solutions were very liable to decomposition at the temperature of the laboratory, about 87°F. The hemogolbin sol and the albumin sol did not also keep well, a bacterial decomposition setting in after a few days.

The first series of experiments were done to determine the stability of the hemoglobin suspension in presence of various other substances. The experimental method consisted in taking 5 c.c. of the sol and mixing it with a 5 c.c. solution containing an electrolyte and the substance whose effect was under investigation. The total volume was always kept 10 c.c. The electrolyte concentration is expressed in moles per litre of the reaction mixture, unless otherwise stated.

From Table I it will be observed that alcohols greatly sensitise the hemoglobin suspension towards $BaCl_2$. With potassium chloride also similar result was obtained. With pure alcohols (up to 60 per cent.) however there was no precipitation of the hemoglobin.

TABLE I.

Effect of Methyl and Ethyl Alcohol.

$BaCl_2$	·001	001	·001	·001
Methyl or ethyl alcohol in c.c.	0	1	2	3
Time in minutes				
0	no effect	slightly turbid	turbid	very turbid
15	do.	do.	ppt.	ppt.
25	do.	do.	ppt.	ppt.
40	do.	strongly turbid	no settling	precipitate settles.

These results agree with those of Jirgensons (*Kolloid Zeit.* 1927, **41**, 331; **42**, 59). In Table II the effect of saponin is shown. The saponin concentration is expressed in grams per 10 c.c. of the reaction mixture.

TABLE II.

$BaCl_2$	·001	·001	·001	·001
Saponin	0	·025	·05	·075
Time in minutes				
0	no effect	immediate turbidity.	immediate ppt.	immediate ppt.
5	do.	does not settle	settles slowly	settles almost immediate
20	do.	do.	complete settling.	complete settling.

From this table it will be observed that saponin considerably sensitises a hemoglobin sol. On further experimentation an interesting fact appeared. The saponin when dissolved in water, itself coagulated the hemoglobin when added in sufficient concentration. When a trace of acid was added to the saponin solution, the precipitation of hemoglobin was very rapid, but in presence of a slight amount of alkali, saponin had no precipitating effect. In Table III the effect of lecithin on hemoglobin is shown.

TABLE III.

$BaCl_2$	·001	·001	·001	·001
Lecithin (c.c.)	0	·5	1·0	1·5
Time (minutes)				
0	no effect	turbid	turbid	turbid
15	do.	slight ppt.	ppt.	ppt.
25	do.	do.	do.	do.

From Table III it will appear that a lecithin sol sensitises the hemoglobin considerably. In alkaline solution however no sensitisation could be observed. The importance of keeping blood alkaline in normal health is thus obvious. In Table IV the effect of egg albumin is shown.

TABLE IV.

$BaCl_2$	·001	·001	·001	·001
Albumin 1·5% in c.c.	0	·5	1·0	1·5
Time				
5′	no effect	slight ppt.	ppt.	ppt.
15′	do.	do.	do.	do.

Table IV shows that albumin also sensitises the hemoglobin sol towards $BaCl_2$. The effect of cholesterol was also studied, but probably due to the very small concentration of the sol, no effect was observed. In Tables V to VIII the effect of saponin, lecithin, albumin and potassium oleate on hemoglobin sol towards potassium chloride is shown.

TABLE V.

KCl	·08	·08	·08
Saponin	0	·025	·05
Time			
0	no effect	turbid	turbid
8′	do.	do.	do.
18′	slightly turbid	do.	settles
30′	turbid	do.	do.
50′	ppt.	settles	do.

TABLE VI.

KCl	·08	·08	·08
Lecithin	0	·5	1·0
Time			
0	no effect	turbid	turbid
7′	do	do	do
15′	do	do	ppt.

TABLE VII.

KCl	·08	·08	·08
Pot. oleate 2½ % c.c.	0	·5	1·0
Time			
0	no effect	no effect	no effect
18′	slightly turbid	do	do
50′	ppt.	do	do
95′	ppt.	do	do

TABLE VIII.

KCl	·08	·08	·08
Albumin	0	·5	1·0
Time			
0	no effect	no effect	no effect
5′	do	turbid	turbid
13′	do	do	do
15′	do	do	ppt.

From these results it will be observed that so far as albumin, lecithin and saponin are concerned, the results are quite similar to that obtained with $BaCl_2$. In the case of potassium oleate however, which could not be tested with $BaCl_2$ owing to a precipitating effect, the results are exactly opposite, namely potassium oleate has a marked peptising effect on the hemoglobin. In connection with these experiments the effect of a bile salt, namely sodium taurocholate was also examined. It was found that this salt has also a distinct though small peptising effect. In Tables IX and X the effect of the mixtures $BaCl_2$+KCl, $BaCl_2$+KOH and KCl + KOH are shown.

TABLE IX.

$BaCl_2$ M/100 c.c.	1·6	1·6	1·6
KCl M/5 c.c.	0	1·0	2·0
Time			
30′	turbid	no effect	turbid
60′	do	do	do
$BaCl_2$ c.c.	1·8	1·8	1·0
KCl c.c.	0	·5	1·0
Time			
30′	turbid	turbid	turbid
$BaCl_2$ c.c.	2·2	2·2	2·2
KCl c.c.	0	1·0	2·0
Time			
0	turbid	no effect	no effect
7′	do	turbid	turbid

TABLE X.

$BaCl_2$ M/5 c.c.	·5	·5	0	·0
KCl M/5 c.c.	0	0	4·0	4·0
KOH final concentration.	0	M/100	0	M/100
Time				
30′	ppt.	no effect	ppt.	no effect

From the results presented in Tables IX and X it will be observed that there is a distinct though small antagonistic action between

$BaCl_2$ and KCl in certain concentrations. With mixtures containing KOH however the antagonistic action is very great, and with greater amounts of KOH the hemoglobin sol could not be flocculated even with a large amount of $BaCl_2$.

So far only the experimental results with barium and potassium chlorides have been given. Experiments were also made with heavy metal cations such as silver, mercury and uranium and the results are substantially the same. Hence these are not given.

Experiments with Lecithin Sol.

In the foregoing pages a number of results have been given on the stability of hemoglobin in presence of various substances. In Tables XI to XV the effect of hemoglobin on lecithin is shown. The experiments have been done exactly in the same way as before. Five c.c. of the lecithin sol was taken and the total volume was 10 c.c.

TABLE XI.

$BaCl_2$ M/5 in c.c.	·2	·2	·2	·2	·2
Hemoglobin in c.c.	0	·5	1·0	1·5	2·0
Time					
5′	no effect	ppt.	no effect	no effect	no effect
17′	do	do	do	do	do
35′	do	do	ppt.	do	do
50′	do	do	ppt.	do	do

TABLE XII.

$BaCl_2$ M/5	·3	·3	·3	·3
Hemoglobin	0	0·5	1·0	1·5
Time				
0	no effect	ppt.	no effect	no effect
5′	do	do	do	do
15′	do	do	ppt.	do
30′	do	do	ppt.	do

TABLE XIII.

$BaCl_2$ M/5	1·0	1·0	1·0	1·0
Hemoglobin	0	0·5	1·0	1·5
Time				
2′	ppt.	ppt.	ppt.	ppt.
5′	do	do	do	do

TABLE XIV.

$HgCl_2$ M/25 in c.c.	·5	·5	·5	·5
Hemoglobin	0	0·5	1·0	1·5
Time				
0	no effect	no effect	ppt.	ppt.
15′	do	do	do	do
25′	do	do	not clear at the top.	clear at the top.
145′	do	do	clear	clear

TABLE XV.

$AgNO_3$ M/5 in c.c.	·2	·2	·2	·2
Hemoglobin	0	·5	1·0	1·5
Time				
0	no effect	slight ppt.	ppt.	ppt.
10′	do	ppt.	do	do
120′	ppt.	top not clear	clear	clear

The results given in Tables XI to XV show that with heavy metal salts the hemoglobin has a sensitising action at all the concentration, but with low amount of barium chloride a distinct maximum

of the sensitising action occurs at a certain concentration of the hemoglobin. This is very similar to the effect of albumin on a ferric hydroxide sol as observed by Brossa and Freundlich (*Zeit. physikal. Chem.*, 1915, **89**, 306). A further study of this point is being made. It is of importance to note in these cases that the hydrophobic sol of hemoglobin distinctly sensitises the hydrophilic sol of lecithin towards metal cations. Hence the original membrane formation may be in part due to a slow precipitation of the lipoids owing to the sensitising action of the albuminoids present.

There are two other constituents of the cell membrane which require investigation, namely cholesterol and protein. The presence of protein as a membrane constituent is very probable but not yet proved. Hence it is not known what the protein is. The experiments conducted with egg albumin plus lecithin in presence of barium and potassium salts have not been decisive as to whether the lecithin is sensitised or not. It is however known that lecithin has an agglutination maxima in a markedly acid region of the hydrogen ion concentration, whereas in presence of albumin this point is shifted towards more neutral region. Also albumin-lecithin mixtures give a sharper flocculation point and forms coarser flakes. (Feinschmidt, *Biochem. Zeit.*, 1912, **38**, 244). It is also known that in some cases neutral albumin gives a precipitation with cholesterol. So far as heavy metals are concerned, the ordinary albumin gives a precipitate with them, and lecithin is also sensitised towards these salts.

With regard to cholesterol, the phenomenon is much simpler. Cholesterol in water gives a hydrophobic sol, and the addition of lecithin considerably stabilises it. A mixture of lecithin and cholesterol acts like a hydrophilic sol (*cf.* Porges and Neubauer, *Biochem. Zeit.*, 1907, **7**, 152; Rona and Deutsch, *ibid*, 1926, **171**, 89). This however, does not necessarily mean that the membrane also behaves like a hydrophile, for the protein would be denatured in the process of membrane formation and hence would give hydrophobic properties to the membrane. The results of Gough (*loc. cit.*) on the agglutinating power of different cations on red blood corpuscles support this (*cf.* however Mines, *Kolloid Chem. Beihefte*. 1912, **3**, 226). As a matter of fact the precipitation or the peptisation of the membrane to be discussed later on appears to be practically irreversible, and hence points to its being more hydrophobic than hydrophilic.

Two further experiments with lecithin will now be given, namely the effects of saponin and sodium taurocholate on the stability of lecithin sols. A few words are however necessary beforehand to show their importance.

It is well known that saponin and bile salts are excellent hemolytic agents, and hemolyse the red blood corpuscles rapidly. It has all along been supposed that their action is entirely on the membrane materials. Thus a solution of the bile salts has apparently a dissolving effect on lecithin and cholesterol and several compounds of lecithin and bile salts have been described in the literature (*cf.* C. H. Boehringer Sohn; *Chem. Zentr.*, 1924, *ii*, 1515; also Long and Gephart, *J. Am. Chem. Soc.*, 1908, **30**, 1312). Fraser and Gardner (*Proc. Roy. Soc.*, 1909, B, **81**, 230) consider that saponin combines with cholesterol. Though no compound formation of lecithin with saponin has yet been reported, yet the action of this substance has also been considered by Bayliss (*General Physiology*, 1918, p. 133) to be similar to that of bile salts. It is of interest therefore to study whether they have any peptising effect on lecithin sols. The following two tables give the results:—

TABLE XVI.

$BaCl_2$ M/5 in c.c.	·5	·5	·5	·5
aponin in grams.	0	·025	·05	·075
Time 0	no effect	no effect	no effect	no effect
10′	ppt.	slight ppt.	do	do
20′	ppt.	turbid	do	do
25′	ppt.	very turbid	less turbid	least turbid

TABLE XVII.

$BaCl_2$ M/5	·5	·5
Sodium taurocholate 1% in c.c.	0	1·0
Time 0	no effect	no effect
10′	ppt.	do
20′	ppt.	do

These results show definitely that lecithin is peptised by saponin and taurocholate. Thus it is possible that the so-called solution of lecithin in bile salts is nothing but a peptisation phenomenon. Consequently it is quite probable that the hemolysis of red blood corpuscles is due to a peptisation of the membrane. It is however, known that both saponin and bile salt hemolysis is inhibited by normal serum. Hence the question naturally arises as to the nature of this antagonistic action, and some investigation has been carried on this point. But before proceeding further a short literature on the subject is given.

It is known from a long time that normal serum inhibits the hemolytic action of saponin and bile salts. Ransom (*Deutsch Med. Woch.*, 1901, p. 194) observed that cholesterol inhibits the action of saponin. and he attributed the inhibitory effect of serum to its cholesterol content. The inhibitory effect of serum on the action of bile salts was studied by Bayer (*Biochem. Zeit.*, 1907, 368). It was found by him that cholesterol has no inhibitory effect, that lecithin produces inhibition but not in quantities that occur in blood, and that the proteins of the blood are responsible for the inhibition. In this connection mention may be made of the observations of Von Eisler (*Zeit. f. Exper. Path. u. Ther.*, 1906, **3**, 296) who stated that serum globulin inhibits the action of Staphalolysin and Tetanolysin, and also those of Liebermann (*Biochem. Zeit.*, 1907, **4**, 25) who found that hemolysis by soaps is prevented by serum albumin. Bayer's researches have in the main been confirmed by Sellards (*Bull. of John Hopkins Hospital*, 1908, **19**, 268). In recent years Ponder (*Proc. Roy. Soc.*, 1923, B, **95**, 42 ; and Kennedy, *Biochem. J.* 1926, **20**, 237) has investigated the inhibitory effect of sera, sugars etc., and has given some interesting conclusions. No one has, it seems, tried to find out whether any relation exists between the amount of hemolyte and the inhibitor in the case of bile salts. Since this inhibitory effect of various substances are important in the study of the permeability relations of the membranes, some experimenets were conducted on the hemolysis of blood corpuscles and the results will be given now.

Experimental.

In the experiments given in the following pages, defibrinated and washed sheep's corpuscles, completely freed from serum by repeated centrifuging with normal saline was used. The R.B.C. was suspended in physiological saline. The solution of serum was prepared in the

same saline in the dilution of 1:10. The egg protein was obtained from a fresh egg and similarly diluted. Neither of the natural proteins were dialysed nor the globulin was separated. The solutions of the bile salts were also made in normal saline and were M/20 strong. In actual experiment 2 c.c. of a 5% suspension of the R.B.C. was taken in a test tube, and in another test tube, known amount of the bile salt solution was mixed with a known amount of serum and calculated amount of normal saline was added to it to bring the combined volume of the R.B.C. suspension and the bile salt solution when mixed together to a standard volume of 10 c.c. The contents of the two tubes were rapidly mixed three times and then allowed to rest in a stand. In majority of the experiments an arbitrary time of 12 minutes was given for complete hemolysis to take place which was determined visually by comparing with a standard hemolysed tube as is usually done in the case of Wassermann reaction. By varying the quantity of the bile salt added, the exact amounts of either glycocholate or taurocholate which would hemolyse completely the 2 c.c. of the suspension in presence of known amounts of serum in 12 minutes were determined. When sufficient care was taken to use always sterilised flasks, test tubes and pippettes the results were quite reproducible. The experiments were done at the laboratory temperature of 87-88° F, but the R.B.C. suspension when not in use was always kept in an ice chest.

In Table XVIII some data are given of the inhibitory effect of normal serum on glycocholate and taurocholate hemolysis. The object was to make a comparative study of the hemolytic powers of these two salts. As far as the authors are aware, this has not been done by any previous investigator. The study would be interesting however, because in the bile excretions the amount of glycocholate is almost double that of taurocholate.

TABLE XVIII.

R. B. C. = 2 c.c. Total volume=10 c.c.

Amount of normal serum added c.c.	Time in minutes required for complete hemolysis in presence of	
	Na glycocholate M/20 1 c.c.	Na taurocholate M/20 1 c.c.
0·00	1	42
0·05	2	...
0·10	4	92
0·20	12	Partial hemolysis only after 2½ hours.
0·30	30	
0·40	69	

The above data show quite conclusively that glycocholate has a much greater hemolytic power than the taurocholate even in the presence of blood serum. The inhibitory power of the serum in very small quantities may also be noted. These facts are important in certain pathological cases such as in jaundice where there is a great secretion of bile salts which are absorbed in the blood stream. The inhibitory action of the serum counteracts the abnormal hymolysis which would otherwise occur due to the excess of glycocholate secreted. In Tables XIX and XX we have summarised the quantitative data on the inhibition of glycocholate hemolysis by means of serum and egg protein.

TABLE XIX.

R. B. C.=2 c.c. Time for complete hemolysis=12 minutes.

Amount of normal serum added in c.c.	Amount of glycocholate reqd. in grams.	Amount of glycocholate neutralised per unit quantity of the serum.
0·0	0·01096	...
0·1	·02435	0·1339
0·2	·04870	·1887
0·3	·07305	·2069
0·4	·09009	·1978
0·5	·11201	·2021
0·6	·13392	·2049

TABLE XX.

Amount of egg protein in c.c.	Amount of glycocholate reqd. in grams.	Amount of glycocholate neutralised per unit quantity of egg protein.
0·0	0·01096	...
0·1	·02678	0·1582
0·2	·06087	·2495
0·3	·08522	·2475
0·4	·10230	·2283
0·5	·12905	·2362
0·6	·14610	·2252

The amount of glycocholate neutralised per unit quantity of the inhibiting substance which has been given in the third column of the above tables has been calculated as follows: Taking for example the data with 0·5 c.c. serum, the excess of glycocholate necessary for hemolysis in presence of this amount of serum is 0·11201—0·01096 grams and hence the amount of glycocholate neutralised per unit quantity of the serum is (0·11201—0·01096)/0·5 gms. Other data have also been obtained in a similar way. The results show the peculiar fact that with both the inhibiting substances, the amount of the hemolysing substance neutralised per unit of the inhibiting substance is almost constant, though the value of the constant differs in the two cases. Rejecting the first data, the mean value of the constant in the case of normal serum is 0·20008 and in the case of egg protein is 0·2373. Egg protein has thus a much greater inhibiting effect than normal serum. The constancy of the ratio points to some sort of chemical interaction between the bile salt and the proteins. It is not known however whether the ratio will remain constant with even greater quantities of the serum, but experiments are in progress. Ponder (*loc. cit.*) has observed in the case of saponin that the quantity of the hemolysing substance neutralised per unit of serum decreases with increase in the concentration of the serum. This points to an adsorption effect of the surface. The data obtained by us are not in variance with this hypothesis, as in many so-called chemical adsorptions such as with gelatine or chrome tanning, a similar thing happens with low concentrations.

These facts naturally raise the important question of the nature of the action exerted by the inhibitory substances like proteins on the hemolysis of the R. B. C. It has already been stated that Brossa and Freundlich (*loc. cit.*) found that albumin sensitises a ferric hydroxide sol, and according to Brossa (*Kolloid Zeit.*, 1923, **32**, 107) serum globulin considerably sensitises negatively charged sols of congo red and benzo-purpurin. Reznikoff (*J. Lab. Clin. Med.*, 1922, **8**, 92) observed that serum albumin has a distinct precipitating effect on colloidal gold in certain concentrations. A similar sensitisation was found by Fischer and Fodor (*Kolloid Zeit.*, 1923, **32**, 279) of colloidal gold in alkaline globulin solution. Reitstötter (*Zeit. f. Immunitätsforsch*, 1920, **30**, 507) has found that albumins from various sera strongly sensitise many sols. Michaelis and Rona (*Biochem. Zeit.*, 1907, **2**, 219; **3**, 109; **4**, 11; **5**, 365; 1908, **7**, 329; **8**, 356; **14**, 476) have shown that sols of ferric hydroxide, mastic

emulsion or kaolin suspension can be sensitised by natural protein solutions. In this class belongs the sensitisation of suspensions of bacteria by blood plasma of pregnant women (Löwenthal and Berthau, *Zentrabl. f. Bakteriol. u. Paresitenkunde*, 1919, I Abt. **83**, 315; Vorschütz, *Pflüg. Archiv.*, 1921, **186**, 290). In all these cases the sensitisation is due to the adsorption of the proteins on the surface of the colloids. The assumption is therefore justifiable that in the case of blood corpuscles also the action of normal serum is one of sensitisation of the colloidal membrane. Inside the body this sensitising action is not evident probably owing to the presence of other hydrophilic colloids like fibrinogen, etc. It is interesting at this place to draw an analogy with an inorganic sol. The agglutinating power of different cations are according to Gough in the case of sheep's R. B. C. in the order $Ce > Th > Ca > K_4Fe(CN)_6$ whilst the coagulating powers of these cations on a copper ferrocyanide sol as determined by us is $Ce > Th > Ca > K_4Fe(CN)_6$ beginning with the highest. Copper ferrocyanide further offers a closer analogy in that it forms membranes with properties very similar to those of the stroma. Thus it is impermeable to sugars and to many metal salts at low concentrations, which is quite analogous to the behaviour shown by the stroma. A recent investigation by Gurchot (*Jour. Phys. Chem.*, 1926, **30**, 88) has shown that the variable permeability of the copper ferrocyanide membrane in presence of different substances is caused by the coagulation or the peptisation of the membrane, and he has drawn attention to the fact that the change in permeability of many plant cells in presence of alcohols investigated by Czapek (*Ber. Deutsch. Bot. Ges.*, 1910, **28**, 159) and the results of Walden (*Zeit. physikal. Chem.*, 1893, **10**, 699) with different organic acids is nothing but due to a coagulation of the membranes. If now a similar view is advanced to explain the permeability of the stroma, the following becomes obvious. We can consider that ordinarily the membrane is in the peptised condition and consists of a fine granular particles the interspaces of which are filled in by the adsorbed aqueous medium, an assumption exactly analogous to that of the copper ferrocyanide membrane. Hence water and many water soluble substances can pass through the membrane. Aqueous solutions of some neutral salts are however not easily permeable because the stroma is polarised owing to the existence of an electrical charge. Salts which have a high coagulative power on the stroma may make the membrane permeable but at the same

time the hemoglobin may be precipitated, whilst those with a comparatively lower coagulating power will be permeable only at high concentrations. This may be the explanation of the fact that the R. B. C. is not permeable to sodium or potassium ions. That with low concentrations of strongly coagulating ions a permanent change occurs in the stroma is shown by the results of Mikwa (*Biochem. Zeit.*, 1924, **149**, 550) who found that small amounts of uranyl acetate actually damage the structure of the cells as is shown by the increased sensitiveness to physiological saline. The impermeability of the sugars is however due to a different cause namely due to negative adsorption, a fact well known in the case of copper ferrocyanide membranes. Assuming then that the hemoglobin does not take any part in the process, hemolysis depends on the following several factors :—

(1) Actual coagulation whereby the membrane material will form coarse flakes, and hence form cracks or holes.

(2) Complete peptisation whereby the whole membrane will get loosened, each particle getting separated from the other.

(3) Mechanical or other form of rupture, such as due to swelling or imbibing of water either by the cell as a whole or by any component of the membrane.

(4) Pure solubility effect, as for example in the case of some organic solvents.

Leaving aside the fourth case for the present, it is clear that the other facts will be dependent on the colloidal condition of the membrane. Thus the effect of blood serum is to protect the membrane from easy peptisability by sensitising it. It has however no actual flocculating action, otherwise hemolysis would occur. The hemolysis by heterologous sera is probably an example in which a new body is present having hemolytic properties. When an actual coagulation takes place, the hemolysis will be evident unless the coagulant is strong enough to coagulate the hemoglobin itself (*cf.* Mond, *Pfluger's Archiv*, 1925, **208**, 574). Thus in the case of mercury salt the following results were obtained with horse blood (*cf.* Lepeschkin, *Med. K. Vet. Nobelinstitut*, 1924, **6**, 1).

(·0001 % $HgCl_2$	Time in minutes	5	15	25	35
	% hemolysed	0	30	80	100

Dunin-Borkowski (*Bull. Acad. Sci., Cracow*, 1908, 494) however

observed that a higher concentration of mercuric chloride than that required to produce complete hemolysis agglutinates the erythrocytes. The behaviour of other heavy metals are of a similar nature.

The acid or alkali hemolysis offers some interesting points. Since the membrane is slightly negatively charged in normal saline, the first action will be to lower the charge, and the lecithin-protein complex will get precipitated. With higher concentration of the acid, the hemoglobin will also be acted on, increasing in size with a consequent change of colour towards brown. The lecithin may also be decomposed with the liberation of fatty acids. In equal concentration, greater action will be exerted by an acid whose ionisation constant is greater. The following data with horse blood (*cf.* Lepeschkin, *loc. cit.*) show the results.

TABLE XXI.

HCl in moles per litre	Time in minutes	5	20	35	120	1000	Colour of hemoglobin.
·0008	% hemolysis	7	10	10	10	10	red
·0010	do.	21	30	30	30	30	red
·0100	do.	80	100	...	...	...	brown

Acetic acid	Time	5	30	40	50	100	1000	colour of hemoglobin.
·0010	% hemolysis	1	2	4	4	4	4	red
·0017	do	11	38	45	45	45	45	red
·0036	do	40	95	100	...	...	...	red
·0100	do	80	100	...	...	...	...	red

From the above results it will be evident that HCl has a greater effect than acetic acid. With regard to the effect of alkali, the first action of it will be to peptise the membrane slightly and thus increase its stability. With higher concentration however the protein portion of the membrane will be dissolved forming salts of the type sodium albuminate, and hence the membrane will become ruptured liberating the hemoglobin (*cf.* Arrhenius and Madsen, *Zeit. physikal. Chem.*, 1903, **44**, 7). In this connection the researches of Eggerth and Mond may be mentioned. Thus Eggerth (*J. Gen.*

Physiol., 1924, **6**, 587) found that when washed sheep's corpuscle is suspended in solutions of p_H 5·2 or more acid, it becomes progressively more electropositive, and this change is coincident with hemolysis. In investigating the hemolytic power of H° and OH' ions, Mond (*Pflug. Archiv*, 1925, **208**, 574) found that a slight decrease in p_H from neutrality causes hemolysis, but on the alkaline side of the neutral point, there is a wide zone of resistance.

The hemolytic action of soaps are also of the same nature as those of the bile salts. These substances also lower the surface tension of water and has a great peptising effect on the membrane materials. Another great similarity of the membranes with that of copper ferrocyanide arises here. Thus it is known from previous researches that sugars sensitise a sol of copper ferrocyanide (Sen, *J. Phys. Chem.*, 1925, **29**, 517). Hence they may be expected to have a similar action on the corpuscle membrane, and hence there ought to be an antagonism between peptising hemolytic agents and sugars. This has actually been observed by Ponder and Kennedy (*loc. cit.*) with a large number of sugars and saponin. These facts, therefore, lead us to the view that *the inhibiting effect of proteins or sugars on saponin, soap or bile salt hemolysis is only a special case of the antagonistic action between a sensitising and a peptising agent in diphasic systems* well-known in colloids, biochemistry and physiology (Sen, *Kolloid Zeit.*, 1926, **39**, 324 ; Clowes, *J. Phys. Chem.*, 1916, **20**, 407 ; Lillie, *Am. J. Physiol.*, 1912, **29**, 372 ; Osterhout, *Plant World*, 1913, **16**, 129; *J. Biol. Chem.*, 1914, **19**, 335).

In conclusion it may be stated that two types of hemolysis have not been discussed, namely by narcotics and by bacteria. So far as narcotics like chloroform, ether, etc., are concerned, it is usually believed that they dissolve the lipoids, but according to Loewe (*Biochem. Zeit.*, 1912, **42**, 207) lecithins, kephalins and related substances give colloidal solutions in choloform, petroleum ether and other solvents. Porges and Neubauer (*Kolloid Zeit.*, 1909, **5**, 193) have pointed out that the precipitation of lecithin in ethyl alcohol solution by $CdCl_2$ and other salts have many points of similarity with a coagulation by electrolyte, and that the ethereal solution also has properties which may be interpreted on the assumption of colloidal solution. Consequently it is quite possible that with narcotics also, the hemolysis is due to an extreme peptisation of the membrane constituents.

So far as bacterial hemolysis is concerned, the work on Staphalolysin and Tetanolysin has been mentioned. Some work has been done by the present authors also, but it is as yet incomplete. It appears however that bacterial hemolysis is a form of destruction of the membrane due at first to a liquefaction of the solid membrane particles and subsequent decomposition of the protein portion. As a matter of fact it appears that the protein constituent is the first thing to be attacked by the bacterias. The phenomenon seems to be analogous to the liquefaction of gelatine gels by many bacilli. The subject will be discussed in a future paper.

Summary.

(1) Hemoglobin forms a negatively charged sol in water. Acids sensitise and alkali peptises the sol. Towards electrolytes it behaves like a typical hydrophobic sol.

(2) Hemoglobin sol is sensitised by alcohols, lecithin, albumin and saponin. In alkaline solution however lecithin does not sensitise the sol. Mixtures like barium chloride and caustic potash and potassium chloride and caustic potash have a considerable antagonistic action. A slight antagonism is also observed with the mixture barium chloride and potassium chloride. Saponin precipitates the sol in slightly acid medium, but not in alkaline medium. Potassium oleate considerably stabilises it towards potassium chloride. Sodium taurocholate has also a slight peptising action.

(3) The lecithin sol behaves like a hydrophilic colloid. With heavy metal salts, hemoglobin has a sensitising action at all concentrations, but with barium chloride, a maximum effect has been observed beyond which the hemoglobin has a peptising action.

(4) Lecithin sol has a strong stabilising action on cholesterol suspensions.

(5) Saponin and the bile salts peptise lecithin. Cholesterol is also peptised by the bile salts.

(6) An experimental study has been made on the inhibitory effect of blood serum and egg protein on glycocholate and taurocholate hemolysis of sheep's R.B.C. It is shown that this effect is only a special case of the antagonistic action between a sensitising and a peptising agent in diphasic systems.

(7) It has been found that glycocholate is a much stronger hemolysing agent than taurocholate.

(8) The mechanism of hemolysis of red blood corpuscles by hemolytes has been discussed. It is shown that the membrane is in the colloidal state, and hemolysis may occur either due to an extreme coagulation whereby cracks will be formed, or due to an extreme peptisation whereby all the particles will go into apparent solution thereby losening the whole structure. In some cases it may be due to a pure osmotic effect where a mechanical rupture of the membrane is possible. This view will explain the following cases:—Hemolysis by hypotonic solutions, by heavy metals, by saponin, soap and bile salts, by narcotics and possibly that by bactricidal action.

It is not however the intention of the present authors to suggest that hemolysis is entirely a colloidal phenomenon, but it is quite probable that in certain cases an ordinary chemical effect such as a scission of the fatty material from the kaphalins by the action of, say acids, may be of determining influence. Also in the case of cobra venom, along with a peptising effect, a fermentative action possibly takes place.

The experiments with the red blood corpuscles were made in the Bacteriological Department of the Bactro-Clinical Laboratory Ltd., Calcutta, and our best thanks are due to the authorities for the free gift of all the necessary materials.

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The Constitution of Rottlerin from Indian Kamala. Part II.

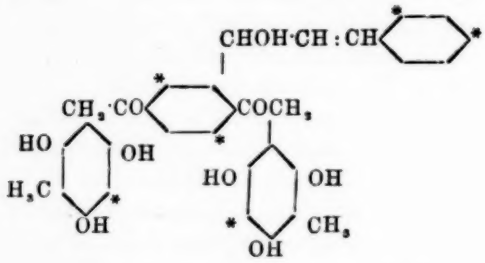
By Sikhibhushan Dutt and Dhanraj Puri Goswami.

In a previous paper by one of the present authors (*J. Chem. Soc.*, 1925, **127**, 2044), rottlerin—the colouring matter of Indian *Kamala*, or *Rori* as it is commonly called in the United Provinces, was isolated and its constitution investigated to a considerable extent by studying the degradation products of the substance and its derivatives under the influence of various chemical reagents. From the results of that investigation it was concluded that rottlerin must have the molecular formula $C_{33}H_{30}O_9$, and that it must contain four benzene nuclei, of which (1) two must be phloroglucinol residues, (2) one must be in the residue $C_6H_5 \cdot CH:CH \cdot C$, and (3) one must be a benzene nucleus containing at least three side-chains. The present investigation was therefore undertaken to elucidate further the constitution of the substance.

The method of attack at the problem, undertaken in the present investigation, was by nitration and bromination of acetyl-, and of methoxy-rottlerin, and subsequent degradation of the nitro-, and bromo-, acetyl-, and methoxy-rottlerin thus formed, by oxidation with neutral potassium permanganate. In almost every case a 2:4-disubstituted benzoic acid was isolated together with some 3:6-disubstituted phthalic and 2:5-disubstituted terephthalic acids. The identification of the latter acids was a matter of considerable difficulty, but was finally overcome by heating with soda-lime, when *para*-disubstituted benzenes were obtained. Thus hepta-acetyl-rottlerin on nitration with fuming nitric acid gave a hexa-nitro-compound, which by oxidation with neutral potassium permanganate gave 2:4-dinitro-benzoic acid together with 3:6-dinitro-phthalic acid and 2:5-dinitro-terephthalic acid. The identification of the latter acids was carried out by heating with soda-lime when *p*-dinitro-benzene was obtained in each case. Hepta-acetyl-rottlerin on bromination with excess of bromine in acetic acid solution under pressure gave a hexa-bromo-hepta-acetyl-rottlerin, which on oxida-

tion with permanganate gave 2:4-dibromo-benzoic acid and a mixture of phthalic and terephthalic acids. Hexa-methoxy-rottlerin on nitration with fuming nitric acid gave a hexanitro compound which on similar oxidation with permanganate gave a mixture of 2:4-dinitro-benzoic acid, 3:6-dinitro-phthalic and 2:5-dinitro-terephthalic acids. In none of the above cases of degradation however could any derivative of phloroglucinol be isolated.

From the experimental results of this paper and those of the previous communication, it seems fairly conclusive that rottlerin has probably the following constitution:—



The positions indicated by asterisks are probably the positions taken up by nitro groups in nitro-acetyl and nitro-methoxy-rottlerin. The structure of rottlerin suggested above is of course provisional subject to further investigation and revision.

Experimental.

Hexanitro-hepta-acetyl-rottlerin, $C_{33}H_{17}O_9(NO_2)_6(C_2H_3O)_7$.—Hepta-acetyl-rottlerin (10 g.) was gradually added to fuming nitric acid (50 c.c., *d* 1·52) in the cold. The acetyl-derivative very rapidly dissolved in the acid, and when the addition was complete, the solution was warmed on the water-bath for about half an hour. On pouring into water the hexa-nitro compound separated in yellow flocks which were filtered off, washed with water and finally crystallised from dilute alcohol.

It is a yellow crystalline substance which is fairly soluble in most of the organic solvents but insoluble in water. On heating it does not melt, but gradually darkens in colour and finally decomposes with evolution of gas. When suddenly heated to a high

temperature it decomposes with a mild explosion. (Found: N, 7·1. $C_{31}H_{17}O_9(NO_2)_6(C_2H_3O)_7$ requires N, 7·4 per cent.).

Hexanitro-rottlerin, $C_{31}H_{24}O_9(NO_2)_6$.—The above nitro-acetyl derivative (5 g.) was heated on the water-bath with a 3% solution of sodium hydroxide (200 c.c.) for about an hour, when the compound completely dissolved and the solution was of a dark red colour. On acidifying with dilute hydrochloric acid the hexa-nitro-compound was precipitated in orange flocks which were collected and crystallised from dilute acetic acid in fine orange needles.

The substance is fairly soluble in most of the organic solvents and to a slight extent in water yielding intense yellow coloured solutions. On heating it does not melt, but at about 200° it gives off gas with explosive violence. When suddenly heated to a high temperature it explodes violently. (Found: N, 9·5. $C_{31}H_{24}O_9(NO_2)_6$ requires N, 10·0 per cent.).

Oxidation of Hexanitro-hepta-acetyl-rottlerin with Potassium Permanganate.—The oxidation was carried out as in the case of hepta-acetyl-rottlerin (Dutt, *J. Chem. Soc.*, 1925, *loc. cit.*) by potassium permanganate in neutral solution. When the reaction was complete, the brown crystalline residue obtained after removal of the oxides of manganese, etc., by sulphur dioxide was filtered off and the mother-liquor also extracted several times with ether. The ether was distilled off and the residue added to the previous residue and the whole crystallised from dilute alcohol. A colourless crystalline acid was obtained, m.p. 179°, which was definitely identified to be 2:4-dinitro-benzoic acid.

The alcoholic mother-liquor, on evaporation to dryness, gave a colourless crystalline residue which, on repeated fractional crystallisation from water, was resolved into two acids melting at 200° and 278° respectively with decomposition. The former was identified to be 3:6-dinitro-phthalic acid while the latter was found to be 2:5-dinitro-terephthalic acid. Each of these two substances on dry distillation with soda-lime gave *p*-dinitro-benzene, m.p. 172°.

Hexabromo-hepta-acetyl-rottlerin, $C_{31}H_{17}O_9Br_6(C_2H_3O)_7$. Hepta-acetyl-rottlerin (10 g.), bromine (25 g.) and glacial acetic acid (20 c.c.) were heated in a sealed tube under pressure at 170° for about six hours. The product was isolated in the form of a brown amorphous powder. It could not be crystallised from any solvent since it is practically insoluble in everything. It does not melt on heating but undergoes decomposition above 300°.

(Found: Br, 35·2. $C_{33}H_{17}O_9Br_6(C_2H_3O)_7$ requires Br, 35·9 per cent.).

Hexabromo-rottlerin, $C_{33}H_{24}O_9Br_6$.—The above brom-acetyl compound (5g. was deacetylated by heating with concentrated hydrochloric acid (150 c.c.) under reflux for about six hours. The hexa-bromo-rottlerin was isolated as a dark brown powder, which could not be crystallised since it is practically insoluble in all the organic solvents. It does not melt on heating. (Found: Br, 45·0. $C_{33}H_{24}O_9Br_6$ requires Br, 45·9 per cent.).

Oxidation of Hexabromo-hepta-acetyl-rottlerin with Potassium Permanganate.—The oxidation was carried out as in the previous instances and from the reaction product, 2:4-dibromo-benzoic acid, phthalic acid and terephthalic acid were isolated and identified.

Hexanitro-hexamethoxy-rottlerin, $C_{33}H_{18}O_9(OCH_3)_6(NO_2)_6$.—Methoxy-rottlerin was nitrated by fuming nitric acid in the same manner as acetyl-rottlerin with formation of a hexa-nitro compound. It crystallises from acetic acid in orange brown glistening needles which decompose on heating. The substance is moderately soluble in most of the organic solvents. (Found: N, 8·61. $C_{33}H_{18}O_9(OCH_3)_6(NO_2)_6$ requires N, 8·2 per cent.).

Oxidation of Hexanitro-hexamethoxy-rottlerin with Potassium Permanganate.—The oxidation was carried out as in the previous instances and from the product of the reaction three substances, namely 2:4-dinitro-benzoic acid, 3:6-dinitro-phthalic and 2:5-dinitro-terephthalic acid were definitely isolated and identified. No phloroglucinol derivative could be detected.

Further work in this direction is in progress.

One of us (D.P.G.) begs to express his best thanks to the Kanta Prasad Trust for a Research Scholarship which enabled him to take part in the investigation.

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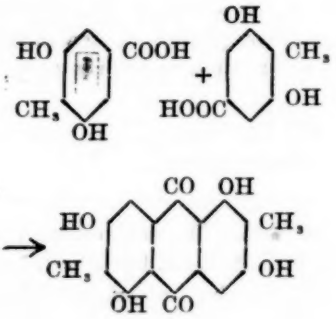
Rubiadin. Part II. Synthesis of 2-Methyl-1:3-dioxyanthraquinone.

By Prafulla Chandra Mitter and Priyalal Gupta.

It has been shown by one of us that rubiadin cannot be 1-methyl-2:4-dioxyanthraquinone (this *Journal*, 1927, **4**, 535) and it appeared to us to be extremely probable that rubiadin has the formula 2-methyl-1:3-dioxyanthraquinone—a formula which has been rejected by Schunck and Marchlewski. (*J. Chem. Soc.*, 1893, **63**, 969). To settle this matter we decided to repeat Schunck and Marchlewski's experiment.

Schunck and Marchlewski condensed 2:6-dioxy-*p*-toluic acid with benzoic acid. In this reaction there is a considerable chance of the formation of a tetraoxy-dimethylanthraquinone by the condensation of two molecules of dioxy-*p*-toluic acid.



This anthrachrysone is likely to interfere with the melting point of the compound sought for. In order to minimise the chance of the formation of anthrachrysone we employed a large excess of benzoic acid. In fact for every molecule of 2:6-dioxy-*p*-toluic acid ten to eleven molecules of benzoic acid were used. In this way a better yield of dioxymethylanthraquinone was obtained and the

formation of anthrachrysone was almost entirely prevented. The condensation product, after removing excess of benzoic acid by steam distillation, was repeatedly crystallised from benzene when 2-methyl-1:3-dioxy-anthraquinone was obtained as bright yellow crystals melting at 290° (which is the melting point of rubiadin itself). Schunck and Marchlewski describe 2-methyl-1:3-dioxyanthraquinone as orange needles melting at 282° and on quickly heating at 290°, and dissolving in sulphuric acid giving a brownish red solution. Our compound melts at 290° and gives with sulphuric acid an orange yellow solution. Rubiadin melts at 290° and gives with sulphuric acid a yellow solution. The acetyl derivative was next prepared by heating with acetic anhydride and a drop of pyridine. On crystallisation from alcohol it melted at 225° which is the melting point of acetyl rubiadin. Schunck and Marchlewski noted 217-218° as the melting point of their derivative. As regards solubility in different solvents (ether, alcohol, benzene, acetic acid, caustic soda, baryta water) our observations are in accord with those of Schunck and Marchlewski.

All these prove conclusively that rubiadin is 2-methyl-1:3-dioxy-anthraquinone. The descrepancies in the melting points of the mother substance and its acetyl derivative observed by Schunck and Marchlewski must have been due to the presence of impurities.

We are now engaged in the synthesis of Munjisthin another hydroxyanthraquinone derivative present in Indian madder which we have reasons to regard as an oxidation product of rubiadin.

Experimental.

Sulphonation of p-*Toluic Acid.*—The sulphonation was effected by the method of Weinreich (*Ber.*, 1887, **20**, 982). *p*-Toluic acid (10 g.) was thoroughly mixed with phosphorous pentoxide (6-7 g.) by shaking in a well-stoppered flask and introduced quickly into a tube. Conc. sulphuric acid (6 c.c.) and 65% sulphuric acid (27 g.) were then added. The tube after being sealed was heated for 3-4 hours at 210-220°, the temperature was then gradually raised to 250° and maintained there for about an hour. After cooling the contents were poured on crushed ice and neutralised with barium carbonate and then boiled. The barium salt of the sulphonic acid occurring in the

filtrate was converted into the potassium salt by adding K_2CO_3 soln. and filtering. The potassium salt was obtained by evaporation of the filtrate.

The alkali fusion was conducted as follows:—The thoroughly powdered potassium salt, about 25 gms. being taken each time, was added in small quantities at a time to fused potash. The addition was made at about 210-220°. The temperature was then gradually raised to about 260° and maintained there until an almost clear melt was obtained. The operation lasts for about an hour and a half.

Separation of 2:6-*Dioxy*-p-*toluic Acid.*—The fused product after extraction with water and acidification was extracted with ether. After distilling off the ether, the residue was dried on a porous plate and then extracted with small quantities of toluene from which 2:6-dioxy-*p*-toluic acid separated on cooling, m.p. 175-176°. The residue insoluble in toluene was identified as mono-oxy-terephthalic acid.

Examination of the Residue: *Hydroxyterephthalic Acid.*—The residue left after extraction with toluene was repeatedly boiled with toluene in which hydroxy terephthalic acid is sparingly soluble. The mass left was next boiled with barium carbonate and filtered, when the barium salt of the acid goes into solution. This was next acidified and extracted with ether. After removing the ether by distillation, the residue was dried on a porous plate. This was next esterified in the usual manner by refluxing on the water-bath with methyl alcohol and conc. sulphuric acid. The ester, was washed with sodium carbonate solution and repeatedly crystallised from methyl alcohol when it was obtained as crystals, m.p. 93°. According to Burkhardt (*Ber.*, 1887, **10**, 146) the m.p. of hydroxyterephthalic acid methyl ester is 94°. (Found: C, 56·88; H, 5·19. $C_{10}H_{10}O_5$ requires C, 57·14; H, 4·76 per cent.)

Condensation of 2:6-*Dioxy*-p-*toluic Acid with Benzoic Acid.*—2:6-Dioxy-*p*-toluic acid (4 g.) was mixed with benzoic acid (32 g.) and concentrated sulphuric acid (about 200 g.) and heated on the oil-bath at 120° for 15 hrs. The reaction product was poured on crushed ice, filtered and the mass, after removal of excess of benzoic acid by steam distillation, was recrystallised from benzene, when 1:3-dioxy-2-methylanthraquinone was obtained as crystals, m.p.

290°. These dried at 100° gave the following results on analysis. (Found: C, 70·39; H, 4·31. $C_{15}H_{10}O_4$ requires C, 70·86; H, 3·93 per cent.).

Acetyl Derivative of 1:3-*Dioxy-2-methylanthraquinone*.—The dioxymethylanthraquinone obtained was heated on the sand-bath with excess of acetic anhydride and one or two drops of pyridine for about six hours. The product was heated repeatedly with alcohol on the water-bath. The residue was crystallised from alcohol when the acetyl derivative was obtained as shining crystals melting at 225°.

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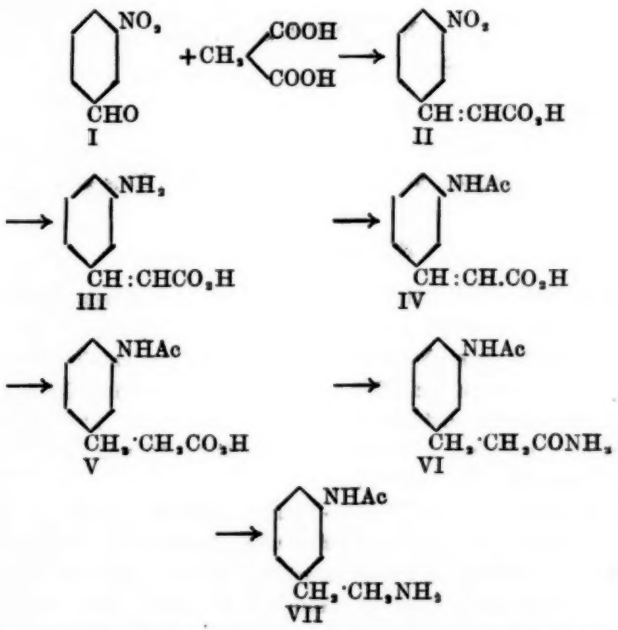
Note on an Attempted Synthesis of β-3-Amino-phenyl-ethylamine.

By Ananta Kumar De.

In connection with certain investigation relating to phenanthrene alkaloids proceeding in this laboratory it became necessary to prepare 3-amino-phenyl-ethylamine.* This interesting substance seems to be unknown and hence it was thought worth while to synthesise it. For this purpose after a number of trials the following scheme was followed:

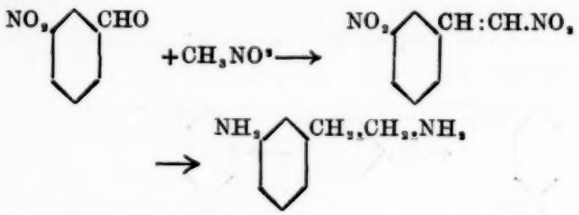


The compound at stage II, is described as a bright yellow substance (Tiemann and Oppermann, *Ber.*, 1880, **13**, 2060), m.p. 196-197° but it is now found to be colourless and melts at 200°-201°. The

* It was the intention to utilise the β-amino grouping for a Pictet and the nuclear NH_2 for a Pschorr synthesis, thereby producing a phenanthreno*iso*-quinoline of the type of *apo*-morphine or dicentrine.

reduction (stage III) is done without difficulty ; the compound melted at 180° (*cf.* Tiemann and Oppermann, (*loc. cit.*), who gives m.p. 180°-181°). The acetylation (IV) is done in the usual way. For reduction (stage V), 2½% sodium amalgam is used. Compounds IV and V are now described for the first time. Unfortunately it was not found possible to prepare the amide either from the chloride of the acid or from its ester.

Hence it was thought that the amine would be better prepared if the condensation product of *m*-nitrobenzaldehyde and nitromethane be reduced.



But unfortunately this could not be done. An attempt was made to reduce it catalytically by palladium and hydrogen. This also failed.

Experimental.

m-*Nitro-cinnamic Acid* (II).—A mixture of *m*-nitrobenzaldehyde (20 g.), malonic acid (25 g.), pyridine (70 c.c.), piperidine (5 c.c.) was heated on the steam-bath for an hour. The product is taken in water (400 c.c.) and is acidified with hydrochloric acid the precipitated nitrocinnamic acid is filtered and well washed. The product crystallises in colourless needles, m.p. 201-202°. (Found : N, 7·6. $C_9H_7O_4N$ requires N, 7·9 per cent.)

m-*Amino-cinnamic Acid* (III).—Ferrous sulphate (180 g.) dissolved in water (450 c.c.) is treated with excess of liq. ammonia. The mixture is warmed on the water-bath to 90° and gradually a solution of nitro-cinnamic acid in ammonia is added with constant shaking. Not more than a few drops are taken in at a time. After the addition of the whole amount, the reaction is continued for 15 minutes on a boiling water-bath. Then it is filtered hot and the filtrate is carefully made very faintly acid with hydrochloric acid. The crystalline precipitate is collected after cooling. It is re-crystallised from alcohol, m.p. 180°. (Found: N, 8·4. $C_9H_9O_2N$ requires N, 8·6 per cent.).

m-*Acetyl-amino-cinnamic Acid* (IV).—A mixture of amino-cinnamic acid (7 g.), acetic anhydride (25 c.c.) and pyridine (1 c.c.) was boiled for 2 hours. To the cold solution water was introduced till a slight turbidity was indicated. Then it was charcoaled, boiled and filtered. The filtrate deposited the acetyl derivative, m.p. 235°. Yield 5 gms. (pure product). (Found: N, 6·75. $C_{11}H_{11}O_3N$ requires N, 6·80 per cent.).

m-*Acetyl-amino-hydrocinnamic Acid* (V).—Acetylaminocinnamic acid (5 g.) was dissolved in 100 c.c. of dilute alkali. The solution was reduced with 2½ % sodium amalgam and was stirred mechanically. During the progress of the reduction, the free alkali in the reaction mixture was neutralised from time to time and at no time it was allowed to react strongly alkaline. The reduction was stopped when hydrogen freely bubbled out of the solution. During the reduction, the temperature of the mixture was not allowed to rise. The reduced acid was obtained on acidification. It was crystallised from hot dilute acetic acid in crusts, m.p. 162°. (Found: N, 6·6. $C_{11}H_{13}O_3N$ requires N, 6·76 per cent.).

It was not possible either to esterify the above acid or prepare an amide.

m-*ω-Dinitrostyrene*.—This compound was prepared by condensing *m*-nitro-benzaldehyde with nitromethane in *cold* absolute alcoholic solution with alcoholic KOH. *m*-Nitrobenzaldehyde (9 g.) and nitro-methane (4·2 g.) were dissolved in alcohol (14 c.c.). The solution was cooled to 0°. This was treated with a solution of KOH (9 g.) in 9 c.c. water and 12 c.c. alcohol, drop by drop. The reaction mixture is thoroughly stirred and at no time the temperature is allowed to rise higher than 5°. At the end of the reaction, the mixture is treated with crushed ice and acidified with well cooled 10% HCl. The precipitated styrene derivative is collected and crystallised from benzene, m.p. 123°-124°. (Found: N, 14·32. $C_8H_6O_4N_2$ requires N, 13·43 per cent.).

It was not found possible to reduce this compound to the amine under investigation.

My thanks are due to Dr. J. N. Rây for his kind interest in the work.

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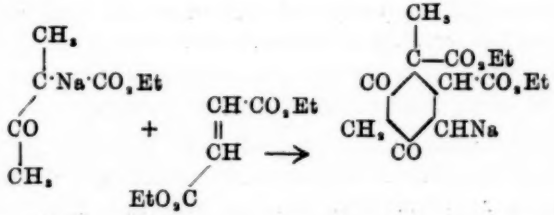
Studies in Michael Condensation.

By Prafulla Chandra Mitter and Asoke Chandra Roy.

The original intention of the present investigation was to condense fumaric ester with methyl-acetoacetic ester by Michael's method, and thereby to prepare ethyl 1-methyl-4:6-*cyclo*hexadione-1:2-dicarboxylate,



which was to be used as the starting material for a particular line of work. Similar condensations have been done, besides Michael, by other workers (Michael, *J. pr. Chem.*, 1887, **35**, 351; 1891, **43**, 395; 1892, **45**, 55; 1894, **49**, 20); Auwers, *Ber.*, 1891, **24**, 317, 2887; 1893, **26**, 364; 1895, **28**, 263, 1131; *Annalen*, 1896, **292**, 147; Vorländer, *Ber.*, 1894, **27**, 2053; *Annalen*, 1897, **294**, 253; Perkin, *Proc.* 1900, 214; Ruhemann, *J. Chem. Soc.*, 1898, **73**, 727, 1006; Hope, *J. Chem. Soc.*, 1912, **101**, 892; Ingold, Shoppee and Thorpe, *J. Chem. Soc.*, 1926, **129**, 1477; Ingold and Shoppee, *J. Chem. Soc.*, 1926, **129**, 1912). The condensing agent used was sodium, either in the metallic state or as the ethoxide, dry or dissolved in alcohol. In view of the different modifications of the process employed by different workers, it was thought advisable to ascertain the most suitable condition for the production of a compound of the above type before using up the costly and difficultly procurable fumaric ester. Fumaric ester was replaced by its easily available homologue, citraconic ester, and methyl acetoacetic ester by acetoacetic ester. Condensation between these two esters had previously been done by Michael. While repeating his experiment, using, however, the modification adopted by Ruhemann and Cunnington (*J. Chem. Soc.*, 1894, **73**, 1006) which is claimed to give very excellent results, we obtained a product different from what Michael had got from the same two

reactants. The result was interesting, and an investigation into the course of the reaction led to conclusions different from Michael's. The interest aroused in the work led to undertaking condensations with other similar substances and kept us confined to Michael's reaction, instead of pursuing the originally planned line.

Condensation between Ethyl Citraconate and Ethyl Acetoacetate.

By the condensation of these two esters with sodium ethoxide in absolute alcoholic solution, Michael obtained a product of the composition, $C_{15}H_{24}O_7$, boiling at 173-174° (26 mm.). Simultaneously there was produced another substance of acidic nature, which however he could not purify and left unstudied. The mechanism of the reaction according to Michael is as follows:

$$COMe.CHNa.COOEt + CMe(COOEt):CH.COOEt \longrightarrow COMe.CH(COOEt).CMe(COOEt).CHNaCOOEt.$$

Instead of using an alcoholic medium for the reaction, we used sodium ethoxide dried in vacuum at 180° according to the method of Ruhemann and Cunnington (*loc. cit.*) with the unexpected result that besides a substance of acidic nature, a liquid was obtained distilling at 182° (6 mm.). Analysis showed that it had the same percentage composition as Michael's liquid, *viz.*, $C_{15}H_{24}O_7$. But the two liquids could not possibly be identical as their boiling points were so widely divergent.

The experiment was then repeated according to Michael's original method, and a liquid was obtained distilling at 164° (8 mm.) apparently identical with what Michael had got.

In both these experiments, the major portion of the reaction product was the substance of acidic nature which was a very viscous oil decomposing on heating, before distillation, even at 4 mm. pressure and showing no tendency to solidification. It could be separated from the neutral oil by shaking with sodium carbonate solution. This will be referred to later on.

When the condensation was done in ethereal medium, with "molecular" sodium, a neutral oil was obtained as before with only a very small quantity of the acidic oil. The neutral oil distilled at 180° (5 mm.) and on analysis was found to be $C_{15}H_{24}O_7$, evidently the same as was obtained by the dry ethoxide method. This was proved subsequently, and henceforth served as a method for obtaining the latter in quantity. In the beginning, however, it was examined separately.

Three liquids, A, B, C were thus obtained in which A seemed to be identical with C.

A—obtained by dry ethoxide method.
B— ,, ,, alcoholate ,,
C— ,, ,, metallic sodium method.

All three liquids were submitted to hydrolysis with dilute hydrochloric acid. By a curious coincidence all of them gave acids melting at 119-120°. But whereas a mixture of the acids obtained from A and C did not depress each others melting points, by admixture of either of them with the acid obtained from B, the melting point was considerably lowered, going down in one case to 93-102°, and in other 100-106°. Thus A and C were the same and different from B.

It then appeared to us that the citraconic ester had undergone intramolecular transformation into itaconic ester under the influence of alcoholic alkaline ethoxide (Hope, *loc. cit.*) On the basis of such an assumption the reaction would be represented as,

$$COMe.CH_2COOEt + CH_2:C(COOEt)CH_2COOEt \longrightarrow$$
$$COMe.CH(COOEt).CH_2.CH(COOEt).CH_2COOEt$$

Ethyl δ-acetobutane-αβδ-tricarboxylate.

assuming the positive negative rule to hold good. This compound on hydrolysis ond splitting off of acetyl group would give butane-αβδ-tricarboxylic acid, $COOH.CH_2.CH_2.CH(COOH).CH_2COOH$. The acid is known and has been first prepared by Auwers, and later on by Perkin, Körner and others. The melting point is variously given by different workers as 122°, 116-120°, 109°-111°, 118°-120. Our substance gave a tribasic acid melting at 119°-120°. This evidence taken in conjunction with the fact that neither α- nor β-methyl tricarballylic acid is obtained, tends to support the assumption made.

Further confirmation was sought by preparing a small quantity of itaconic ester itself and condensing it with acetoacetic ester with "molecular" sodium suspended in ether. An oil was obtained distilling at 166° (8 mm.) closely agreeing with the temperature of distillation of what has been termed Michael's oil, *viz.*, 164° (8 mm.). As previously stated the condensation of citraconic ester by the same method gave an oil boiling at 180° (5 mm.). This experimental result also supported the assumption that in alcoholic ethoxide medium, citraconic ester was converted into itaconic ester in the

course of condensation, and that in absence of alcohol the ester condensed in the normal fashion even in the presence of sodium ethoxide.

Our assumption was still further coroborated by hydrolysing the oil obtained with itaconic ester. An acid was obtained melting at 118-120°, the melting point remaining unchanged on admixture with the acid obtained from Michael's oil.

The condensation of citraconic ester and acetoacetic ester with sodium ethoxide in alcoholic medium and subsequent hydrolysis were thus proved to proceed as follows:—

$$COMe.CH_2.COOEt + CMe(COOEt):CH.COOEt \longrightarrow$$
$$COMe.CH_2.COOEt + CH_2:C(COOEt).CH_2COOEt \xrightarrow{(H_2O)}$$
$$COMe.CH(COOEt).CH_2CH(COOEt).CH_2COOEt \longrightarrow$$
$$COOH.CH_2.CH_2.CH(COOH).CH_2COOH.$$

Turning now to the other liquid obtained by the dry sodium ethoxide or "molecular" sodium method, this in all probability is a normal condensation product. There are two possible formulae for the liquid COMe.CH(COOEt).CMe(COOEt)CH_2COOEt (I) and COMe.CH(COOEt).CH(COOEt)CHMe(COOEt) (II). The compound loses CO_2 during hydrolysis. Of the two alternative formulae, formula (I) contains a carboxyl group attached to a tertiary carbon atom, and a compound with this formula has a greater chance of losing CO_2 than the compound with formula (II), and we are therefore justified in adopting formula (I).

$$COMe.CH_2.COOEt + CMe(COOEt):CH.COOEt$$
$$\longrightarrow COMe.CH(COOEt).CMe(COOEt).CH_2.COOEt$$

Ethyl β-methyl-γ-aceto-propane-αβγ-tricarboxylate.

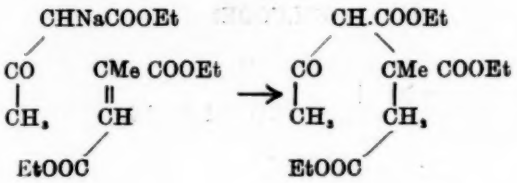
$$H_2O \longrightarrow COMe.CH(COOH).CHMe.CH_2COOH.$$

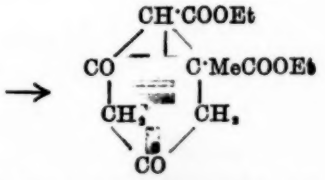
β-Methyl-γ-acetopropane-αγ-dicarboxylic acid.

The formula for the tricarboxylic ester given above is also in agreement with Michael's rule. In fact this is the formula which Michael ascribed to the liquid previously referred to, which we have proved to possess a different configuration.

With regard to the substances of acidic nature mentioned previously, we assumed them to be ring structures obtained from the open-chain compounds by internal acetoacetic ester condensation.

(Meyer and Jacobsen: "Lehrbuch der organischen Chemie" II, i, p. 817). Thus citraconic ester and acetoacetic ester would give



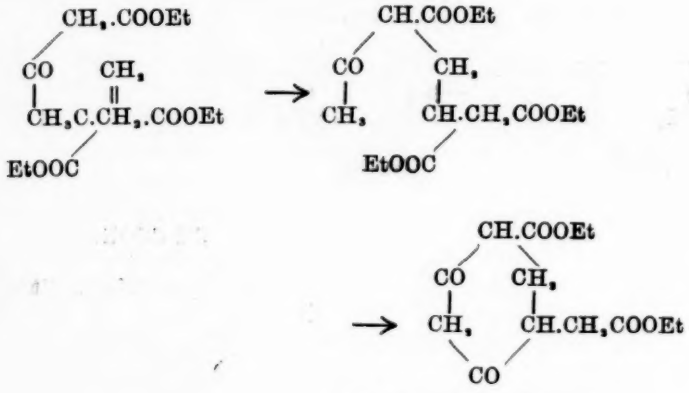


Ethyl 2-methyl-4 :6-*cyclo*-hexadione-1 : 2-dicarboxylate.

The viscous oil obtained from the product of condensation of acetoacetic and citraconic esters (with dry sodium ethoxide or molecular sodium) by shaking with sodium carbonate and subsequent acidification, extraction with ether, drying etc., could not be distilled even at low pressures. Vigorous decomposition ensued and the substance was completely destroyed. It did not solidify after being kept in a vacuum desiccator for about a month. Michael, too, in his experiment met with a similar semi-solid oil and stated that he could not purify or isolate the product. We tried to hydrolyse the substance with acid and alkali of different strengths, but only obtained small quantities of solid mixed with tarry matter which were found to be extremely difficult to purify. The present specimen prepared melted between 190° and 197°. As large quantities of the substance were lost by this process, we took recourse to a different means. The oil was converted into the semicarbazone and this was purified and analysed. The semicarbazone is not formed very readily, but requires three or four hour's heating on the water-bath. But the compound is obtained fairly pure, can easily be further purified and the yield is moderate. Analysis of the compound corresponded to $C_{14}H_{21}N_3O_6$ that is, to the mono-semicarbazone of the β-diketone. The compound melted at 237°.

The ring compound obtained from itaconic ester (or citraconic

ester in alcoholic medium), sodium and acetoacetic ester, would then be formed as follows:—



1-Carbethoxy-4 :6-*cyclo*hexadione-3-acetic acid ethyl ester.

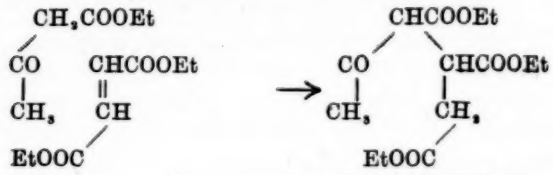
The semicarbazone of the viscous oil was prepared, and estimation of the nitrogen-content showed that it was the mono-semicarbazone of the above ring compound. The melting point is 251°.

Condensation between Fumaric and Aceto acetic Esters.

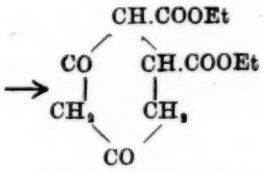
Condensation between these two esters with sodium-ethoxide had previously been done by Ruhemann and Browning (*J. Chem. Soc.*, 1898, **73**, 727). They obtained a liquid distilling at 187°—188° (11 mm.). We obtained a light oil and a heavy viscous substance, the former distilling at 145° (4 mm). The divergence between the conditions of distillation of the two liquids at first sight appears to be too great for the liquids to be identical, but this is not surprising when we consider that the same liquid had been prepared in a different way by Emery (*Ber.*, 1890, **23**, 3787) who gives the distilling temperature as 175° (9 mm). That is, the fall of boiling point with fall of pressure seems to be abnormally great.

In this case there is no possibility of isomeric conversion, and as a matter of fact the light oils obtained by condensation either with the aid of sodium ethoxide in alcoholic solution or with metallic sodium suspended in ether were the same.

The two products formed in the reaction are :—



Ethyl γ-aceto-propane-αβγ-tricarboxylate.

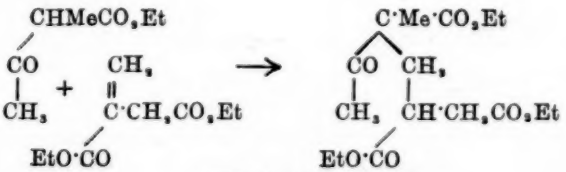


Ethyl 4 :6-*cyclo*hexadione
-1 :2-dicarboxylate.

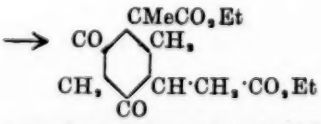
The open-chain compound was analysed, and the nitrogen content of the mono-semicarbazone of the ring compound determined. The results were as expected.

Condensation between Ethyl Citraconate and Ethyl Methylacetoacetate.

(*a*) With sodium ethoxide in alcoholic solution two products were obtained as before and their modes of formation are represented as :—



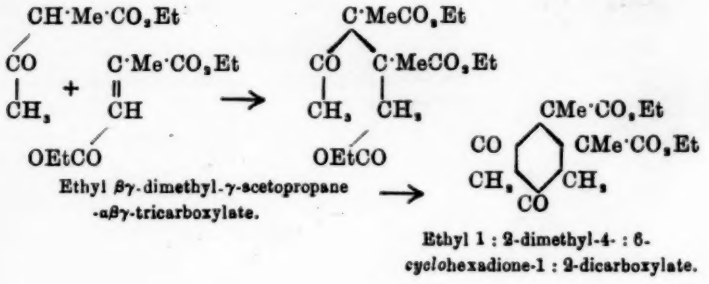
Ethyl δ-aceto-δ-methylbutane
-αβδ-tricarboxylate.



1-Carbethoxy-1-methyl-4 : 6-*cyclo*hexadione
-3-acetic acid ethyl ester.

The open chain compound boils at 175° (9 mm.), and the mono-semicarbazone of the ring compound melts at 247°.

(*b*) With *dry* sodium ethoxide—the two compounds are represented thus:—



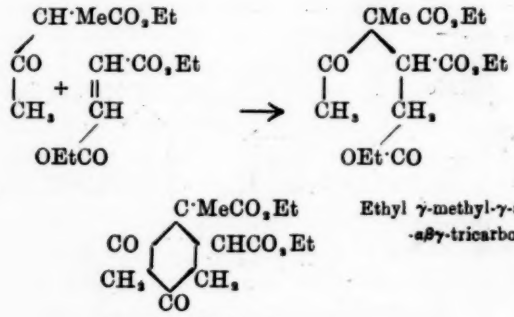
Ethyl βγ-dimethyl-γ-acetopropane -αβγ-tricarboxylate.

Ethyl 1 : 2-dimethyl-4- : 6-*cyclo*hexadione-1 : 2-dicarboxylate.

The chain compound boils at 185° (9 mm.) and the mono-semicarbazone of the ring compound melts at 235°.

Condensation between Ethyl fumarate and Ethyl Methylacetoacetate.

The two products obtained are given in the following representation of the reaction:—



Ethyl γ-methyl-γ-acetopropane -αβγ-tricarboxylate.

Ethyl 1-methyl-4 : 6-*cyclo*hexadione-1 : 2-dicarboxylate.

The open chain compound boils at 149° (5 mm.), and the mono-semicarbazone of the ring compound melts at 240°.

Condensation between Ethyl Citraconate and Ethyl Cyanacetate.

Perkin and Thorpe (*J. Chem. Soc.*, 1899, **75**, 52) have effected condensations on similar lines between cyanacetic ester and dimethylacrylic ester and obtained two products, a neutral liquid and an acidic viscous substance which could not be distilled even under diminished pressure. The neutral liquid was the normal condensation product, $CN.CH(COOEt).CMe_2.CH_2COOEt$ while the acidic oil decomposed on distillation at ordinary pressure losing carbon dioxide and giving a product which they proved conclusively to have the formula, $CN.CH_2.CMe_2.CH_2COOEt$ so that the original acidic liquid, which of course, being in the crude condition, could not be analysed, was given the formula $CN.CH(COOH).CMe_2.CH_2COOEt$.

Later on, Howles, Thorpe and Udall (*J. Chem. Soc.*, 1900, **77**, 943) condensed *iso*propyl acrylic ester with cyanacetic ester and came to similar conclusions. The condensing agent used in both the experiments was sodium ethoxide in alcoholic solution.

Parallel results were obtained with the compounds we used. We got a neutral oil boiling at 170° (5 mm.), and an acidic viscid substance which decomposed on heating into carbon dioxide and a mobile liquid boiling at 286° under ordinary pressure. There was however this difference with Perkin and Thorpe's results that the citraconic ester underwent conversion, as was to be expected, into itaconic ester during the course of condensation. This point was made sure by using finely divided sodium suspended in benzene (ether being rendered unsuitable by the advent of the hot season) as the condensing agent. Following the usual procedure, the reaction yielded only one product, *viz.*, a neutral liquid distilling at 190° (6 mm.), evidently different from the neutral liquid obtained by the former method. The difference was also proved by hydrolysis.

Thus, when alcoholic sodium ethoxide is the condensing agent, the reaction would be represented as:

$CN.CH_2COOEt + CH_2:C(COOEt).CH_2COOEt$

$\rightarrow CN.CH.(COOEt).CH_2.CH(COOEt).CH_2.COOEt$ (A)

$\rightarrow CN.CH(COOH).CH_2CH(COOEt).CH_2COOEt$ (B)

$\rightarrow CN.CH_2.CH_2.CH(COOEt).CH_2COOEt.$ (C)

Ethyl δ-cyano-butane-αβ-dicarboxylate.

Both A and C gave, after hydrolysis with dilute hydrochloric acid, the same butane $\alpha\beta\delta$-tricarboxylic acid also prepared in a different way as stated previously.

The formation of an acid (B) by the condensation of two neutral esters appears to be curious. The explanation advanced by Thorpe (*J. Chem. Soc.*, 1900, 77, 923) is that the sodium compound of cyanacetic ester reacts in the form—CN.CH:C(OEt).ONa.

The series of reactions, when the other reactant is dimethylacrylic ester, would then be represented as follows:

$$\begin{aligned}
&\text{COOEt.CH:CMe}_2 + \text{CN.CH:C(OEt)ONa} \\
&\longrightarrow \text{COOEt. CH}_2\text{. CMe}_2\text{.C(CN):C(OEt).ONa} \\
&\text{H}_2\text{O} \\
&\longrightarrow \text{COOEt. CH}_2\text{CMe}_2\text{.CH(CN).C(OH).OEt.ONa} \\
&\longrightarrow \text{COOEt.CH}_2\text{.CMe}_2\text{.CHCN.COONa} \\
&\text{Acidifying} \\
&\longrightarrow \text{COOEt.CH}_2\text{.CMe}_2\text{.CH(CN).COOH}
\end{aligned}$$

By using sodium suspended in benzene as the condensing agent, practically one product is formed from citraconic and cyanacetic esters. The acidic product, though formed, is only slight in quantity. The neutral liquid obtained had the same percentage composition as the neutral liquid mentioned just before. This was, of course, according to expectations. The formula for this liquid is CN.CH (COOEt).CMe(COOEt).CH_2COOEt (ethyl β-methyl-γ-cyanopropane-$\alpha\beta\gamma$-tricarboxylate.)

On hydrolysis it gave an acid having the percentage composition $C_7H_{10}O_6$ melting at 160°-162°, evidently β-methyl-tricarballylic acid (m.p. 164°).

Condensation between Ethyl Fumarate and Ethyl Cyanacetate.

The neutral and acidic products of the reaction have the formulae given below:

$$\begin{aligned}
&\text{CN.CH}_2\text{.COOEt} + \text{CH(COOEt):CH.COOEt} \\
&\longrightarrow \text{CN.CH(COOEt). CHCOOEt.CH}_2\text{COOEt (neutral product)}
\end{aligned}$$

Ethyl γ-cyanopropane-$\alpha\beta\gamma$ tricarboxylate.

and CN. CH (COOH). CH (COOEt). CH_2COOEt (acidic product).

γ-Cyanopropane-$\alpha\beta\gamma$-tricarboxylic acid $\alpha\beta$-diethyl ester.

Hydrolysis with dilute hydrochloric acid yielded an acid melting at 159°-160° which is without doubt tricarballylic acid, the accepted melting point of which is 160°-162°.

The neutral oil boiled at 167° (7 mm.) and the acidic compound decomposed on distillation into carbon dioxide and a mobile liquid boiling at 282°. The latter is evidently $CN.CH_2.CH(COOEt).CH_2COOEt$ (ethyl γ-cyano-propane αβ-dicarboxylate).

Experimental.

Preparation of Citraconic Ester.—The method adopted was a slight modification of the process prescribed by Piutti (*Ber.*, 1898, **31**, 2039). Citric acid (900 g.) is melted in a wide basin and the molten mass kept at a temparature of 150° for an hour to dehydrate the acid. It is then quickly poured into a one litre distilling flask with a short neck and rapidly distilled over a ring-burner. At first water and carbon dioxide escape, then vigorous decomposition begins with an irritating smell which afterwards becomes more moderate. The liquid distilling over 180° is collected and then redistilled. Citraconic anhydride is obtained distilling at 210°. Yield 110 g.

The citraconic anhydride is esterified with alcohol (700 c.c.) and strong sulphuric acid (70 c.c.). Yield 150 g.

Condensation between Ethyl Citraconate and Ethyl Acetoacetate.

(*a*) Using dry sodium ethoxide :—

Citraconic ester (18·6 g.), acetoacetic ester (13 g.) and about 2 gm. of finely powdered sodium ethoxide dried in vacuum at 180°, are heated on an oil-bath at about 130° in a flask provided with a reflux tube for about 6 hours. After cooling water is added. An oil is thrown down, but a large portion of the reaction product remains dissolved in water as the sodium compound. A little ice is added and the oil extracted twice with ether. The residual liquid is acidified, when further separation of oil takes place which is also extracted twice with ether. If in the first place no water is added but the reaction mixture is at once acidified and extracted with ether, the ethereal extract contains both the oils which are separated by shaking with sodium carbonate solution. The second or acidic constituent thus removed is recovered by acidification and extraction with

ether. Both the ethereal extracts are dried with anhydrous sodium sulphate, and the ether distilled off. The first product which is a comparatively light oil is the open-chain compound, α-acetyl-β-methyltricarballylic ester, $MeCO.CH(COOEt)CMe(COOEt)CH_2COOEt$, the sodium compound of which is apparently decomposed by water. It is purified by two distillations under diminished pressure when a colourless liquid is obtained distilling constantly at 182° (6 mm). The yield is 10—12 g. (Found: C, 56·87 ; H, 7·60. $C_{15}H_{24}O_7$ requires C, 56·96 ; H, 7·59 per cent.).

The viscous portion of the reaction products weighs about 15 g. It decomposes vigorously on heating even in high vacuum, and hence it could not be distilled.

For the preparation of the semicarbazone it is necessary to heat the mixture of the substance with semicarbazide hydrochloride and sodium acetate for four hours. Crystallised from water. The analytical data shows that it is the mono-semicarbazone of 1-methyl- 3:5-*cyclo*hexadione-1:6-dicarboxylic ester. (Found: C, 51·20 ; H, 6·60; N, 12·61. $C_{14}H_{21}N_3O_6$ requires C, 51·37 ; H, 6·42 ; N, 12·84 per cent.).

(*b*) Using sodium ethoxide in alcoholic solution:—

Sodium (4·6 g.) is dissolved in absolute alcohol (50 c.c.) in a round-bottomed flask fitted with a reflux condenser. After cooling acetoacetic ester (26 g.) is added and then citraconic ester (37·2 g.). The mixture is heated on the water-bath for about 8 hours. The flask is cooled and then water added. The two products of the reaction are separated as in the previous case. The neutral ester δ-aceto-butane-αβδ-tricarboxylic ester is obtained in an yield of about 20-25 g., b. p. 164°/8 mm. (Found : C, 56·75. ; H, 7·32. $C_{15}H_{24}O_7$ requires C, 56·96 ; H, 7·59 per cent.).

Thus the percentage composition is the same as that of the liquid prepared by the dry ethoxide method.

The crude heavy product of the reaction weighs nearly 30 g. The semicarbazone is prepared in the way described before; m. p. 251°. Analysis showed that is the mono-semicarbazone of the cyclic derivative, 4:6-*cyclo*hexadione-1-carbethoxy-3-acetic acid ethyl ester. (Found: N, 12·55. $C_{14}H_{21}N_3O_6$ requires N, 12·84 per cent.).

(*c*) With metallic sodium in ethereal medium :—

Sodium (2·3 g.) melted under boiling xylene is shaken to a fine powder. After cooling the xylene is replaced by dry ether (75 c.c.).

The reaction is carried out in a stout round-bottomed flask fitted with a reflux condenser. Acetoacetic ester (13 g.) is then added in three or four instalments avoiding elevation of temperature. After about an hour citraconic ester (18·6 g.) is added all at once. The reaction is at first vigorous, but afterwards slows down and is to be kept in progress by carefully warming it on a water-bath. Complete solution of the white particles takes place in 3-4 hours. It is very difficult to start the reaction once it has stopped, and hence from the first spontaneous commencement of the reaction it should be kept going, without allowing the flask to attain room temperature.

The reaction product is decomposed by adding water, when the latter goes into the ethereal layer. This is treated in the usual way. The boiling point of the liquid is 180° (5 mm). The liquid is apparently identical with α-acetyl-β-methyl tricarballylic ester prepared by method (*a*).

Hydrolysis.—The volatile parts of the products obtained by the three methods were submitted to the same process of hydrolysis.

About 10 g. of the tricarboxylic ester are heated on a water-bath with dilute hydrochloric acid (1 : 2, 75 c. c.) for five hours. The liquid is then directly evaporated as far as possible on the water-bath. The pasty mass solidifies on cooling. The crude solid is then purified by two recrystallisations from a mixture of ethyl acetate and petroleum ether. Yield of the pure product is about 1·5 g. (theoretical yield about 6 g.). The melting point of the pure product in each of the three cases is 19-120°. The acids were mixed, two and two, and melting point of each mixture determined. A mixture of acids from the dry ethoxide method and metallic sodium method showed no change in melting point. But when mixed with the acid obtained by the sodium alcoholate method, the former melted at 93-102° and the latter between 100° and 106°. This proved the identity of the first two acids and their difference from the third.

On hydrolysing α-acetyl-β-methyl-tricarballylic ester a dibasic acid of the formula $C_8H_{12}O_6$ is formed. (Found : C, 50·70; H, 6·74. $C_8H_{12}O_6$ requires C, 51·06; H, 6·38 per cent.). On titration with baryta the acid was found to be dibasic. 0·0580 gm. requires 21·1 c.c. of 0·029*N* baryta. Calculated for a dibasic acid—21·3 c.c. On hydrolysing δ-acetylbutane-αβδ-tricarboxylic ester, a tribasic acid of the formula $C_7H_{10}O_6$ is formed. (Found : C, 44·01; H, 5·49. $C_7H_{10}O_6$ requires C, 44.21 ; H, 5·26 per cent.). On titration with

baryta it was found to be tribasic. 0·0433 g. requires 22·95 c.c. of 0·029 *N* baryta. Calculated for a tribasicacid—23·43 c.c.

Condensation between Ethyl Fumarate and Ethyl Acetoacetate.

The reaction is carried out in alcoholic solution according to the process given previously. In this case the mixture is heated for five hours instead of eight. Starting with fumaric ester (34·4 g.) about 16 g. of pure open-chain compound are obtained and nearly 30 g. of the crude ring compound. The boiling point of the former is 145° (4 mm.). The same product, *viz.*, α-acetyltricarballylic ester is also obtained by conducting the condensation in ethereal medium with molecular sodium.

The *open-chain* compound. (Found: C, 55·02; H, 7·32. $C_{14}H_{22}O_7$ requires C, 55·21 ; H, 7·52 per cent.).

The *ring* compound: (Found: N, 13·55. $C_{13}H_{19}O_6N$ requires N, 13·41 per cent.).

Condensation between Ethyl Citraconate and Ethyl Methylacetoacetate.

The procedure employed either when the reaction is done in an alcoholic medium or with dry sodium ethoxide is as described before except that the duration of heating is prolonged to twelve hours in both cases. Starting with citraconic ester (18·6 g.) the yield of the open-chain compound in the first case is 15·5 g. (b. p. 175°/9 mm.). and in the second it is about 12 g. (b. p. 185°/9 mm).

The analytical results are as follows:—

(*a*) Alcoholate method—

(*i*) *Open-chain* compound. (Found: C, 57·97; H, 8·00. $C_{14}H_{22}O_7$ requires C, 58·18 ; H, 7·87 per cent.).

(*ii*) *Semicarbazone* of the ring structure, m.p. 247°. (Found: N, 12·18. $C_{14}H_{23}N_3O_6$ requires N, 12·31 per cent.).

(*b*) The corresponding analytical results for the products obtained by the dry sodium ethoxide method are:

(*i*) *Open-chain* compound. (Found: C, 58·00; H, 8·11 per cent.).

(*ii*) Semicarbazone, m.p. 225°. (Found: N, 12·16 per cent.). The theoretical figures are the same as in (*a*).

Condensation between Ethyl fumarate and Ethyl Methylacetoacetate.

The duration of heating is about 8 hours, and 17·2 g. of fumaric ester gave 12 g. of the neutral condensation product. The boiling

point is 149° (5 mm.). (Found: C, 56·72; H, 7·73. $C_{11}H_{14}O_4$ requires C, 56·96; H, 7·59 per cent.).

Mono-semicarbazone of the ring compound melts at 240°. (Found: N, 12·60. $C_{14}H_{21}N_3O_6$ requires N, 12·84 per cent.).

Condensation between Ethyl Citraconate and Ethyl Cyanacetate.

(*a*) *In alcoholic medium*:—

Sodium (2·3 g.) is dissolved in absolute alcohol (25 c.c.) and citraconic ester (11·3 g.) added in three or four portions to avoid too much elevation of temperature. The white crystalline sodio-cyanacetic ester forms almost a cake within the reaction flask. Citraconic ester (18·6 g.) is then added and the mixture heated on the water-bath for 7-8 hours, cooled, acidified with dilute hydrochloric acid, and then extracted with ether. The ethereal layer contains two products from which the acidic constituent is separated by shaking with alkaline carbonate solution. It is reprecipitated by acid and extracted with ether. The two ethereal extracts are dried and freed from ether. The neutral ester is purified by distillation under diminished pressure (b.p. 170°/5 mm.). Yield—10 gms. The acidic viscous liquid cannot be distilled without decomposition. It is heated at ordinary pressure whereby CO_2 escapes, as can be readily tested by lime water, and a light liquid is obtained which distills at 286°, under atmospheric pressure. Yield—10 gms. (Found: (neutral liquid) C, 55·92; H, 7·30; N, 4·48. $C_{14}H_{21}O_6N$ requires C, 56·19; H, 7·02; N, 4·68 per cent.).

Analysis of the second liquid.—(Found: C, 55·90; H, 7·61; N, 6·00. $C_{11}H_{17}O_4N$ requires C, 56·15; H, 7·49; N, 6·17 per cent.).

(*b*) *In benzene medium.*—The reaction is carried out in the same way as when ether was used in some of the experiments described previously, with this difference that it was done on a water-bath. Citraconic ester (18·6 g.) gave about 30 g. of a liquid distilling at 190°/6 mm. (Found N, 4·52. $C_{14}H_{21}O_6N$ requires N, 4·68 per cent.).

Hydrolysis:—The three liquids thus obtained by the two methods were hydrolysed with dilute hydrochloric acid. Ten g. of the liquid were heated on the water-bath with 70 c.c. of dilute HCl (1:1) for six hours. Ammonium chloride and a nitrogen-free acid are formed in each case. The liquid is evaporated to a small volume, cooled and

extracted with ether. On evaporation of the ether, a solid remains which may be recrystallised from ethyl acetate and a little ligroin. The yield is very small, about 0·5 g. in each case, owing to the difficulty of extracting them from water in which they are extremely soluble. The acids obtained from the first two liquids melted at 118-120° and were proved identical with butane $\alpha\beta\delta$-tricarboxylic acid prepared as stated before by a different method, by mixed melting point method. The acid from the third liquid melted at 160-162°. This is β-methyl tricarballylic acid whose m.p. is given as 164°.

Condensation between Ethyl Fumarate and Ethyl Cyanacetate.

The experimental procedure is the same as in the last experiment. The reaction is carried out in alcoholic solution. Two products were obtained as before, the neutral liquid boiling at 167° under 7 mm. and the acidic portion decomposed on heating, evolving CO_2 and giving a liquid of b.p. 282°. The yields from 17·2 g. of fumaric ester were respectively 12·5 g. and 11 g. when the heating was for 6 hours. (Found (neutral liquid): N, 4·70. $C_{11}H_{15}O_6N$ requires N, 4·91 per cent.).

Product obtained from acid liquid: (Found: N, 6·32. $C_{10}H_{13}O_4N$ requires N, 6·57 per cent.).

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Studies in Photo-Chemical Reactions. Part III. The Influence of Polarised Radiations on Certain Photo-Chemical Reactions.

By S. S. Bhatnagar, Hira Lal Anand and Amar Nath Gupta.

Semmens (*J. Soc. Chem. Ind.*, 1923, **42**, 954) found that the hydrolysis of starch grains proceeds much more rapidly in polarised light than in heterogeneous light. Baly and Semmens (*Proc. Roy. Soc.*, 1924, **97B**, 250) noticed that plane polarised light caused a marked acceleration in seed germination and formation of flower but no effect was observed on vegetative growth. They also showed that starch was completely hydrolysed in weak diastase solution when exposed to polarised light, while only a slight serration of the grains took place in ordinary light.

Jones (*Ann. Bot.*, 1925, **39**, 651) was unable to repeat the experiments on the hydrolysis of starch in the presence of gelatine solution. Baly and Semmens (*Nature*, Dec. 5, 1925, 817) attributed this failure to an experimental defect in Jones's experiments.

Recently Semmens repeated her experiments on the hydrolysis of starch in small flasks using light polarised by the scattering of colloidal particles of taka-diastase and she again got positive results. Bhatnagar and Lall (*Nature*, 27th Feb., 1926) showed that *V. cholerae* and *B. typhosus* grow more rapidly in polarised light than in ordinary light of the same intensity.

Experiments on the effects of polarised radiations on metabolic activity in rabbits and guinea-pigs by the same workers along with Mathur yielded exactly similar results. On this basis they gave a theory of the rise in temperature in the afternoon in normal individuals as well as in certain pathological conditions (*Nature*, 3rd July, 1926, 11).

In light of the above facts, it becomes important to examine whether the character of light with respect to its state of polarisation has any effect on photo-chemical reactions.

It is generally recognised that the frequency and intensity both affect the photo-chemical equilibrium, but the role of polarisation has not been studied except by Weigert (*Ber. deutsch. Phys. Ges.*, 1919, **21**, 482), and Zocher and Coper (*Zitzungsber. Preuss. Akad. Wiss.*, 1925, **23**, 426). Cotton and Mouton also showed that the absorption of the two components of circularly polarised light by copper tartrate differ considerably.

Investigations on the above lines evidently ought to give valuable information regarding the mechanism of the photo-chemical reactions, and if the results obtained are similar to what has been observed in the case of certain bio-chemical reactions, it will be possible to apply the knowledge obtained from the latter experiments to the elucidation of the former, as the chemical reactions studied here are certainly simpler and better understood than the complex bio-chemical reactions studied by previous investigators.

Since the well-known photo-chemical reactions can be divided into two classes, *viz.* (1) reactions which constitute homegeneous systems and (2) reactions constituting heterogeneous systems, it was considered desirable to include in the present investigation examples from both the classes.

The following reactions were chosen as representing the first class:—

(*i*) The reduction of mercuric chloride to calomel by ammonium oxalate in presence of light, which proceeds according to the following equation:

$$2HgCl_2 + (NH_4)_2C_2O_4 = Hg_2Cl_2 + 2NH_4Cl + 2CO_2.$$

Winther (*Zeit. Wissen. Phot.*, 1909, **7**, 409) has shown that the light sensitivity of this reaction is accelerated by ferric ions.

(*ii*) The change of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid in acetone solution.

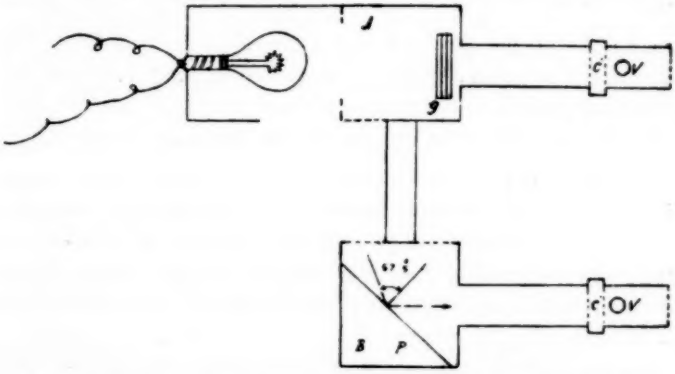
(*iii*) The photo-decomposition of hydrogen peroxide.

Of the second class of photo-chemical reactions the interaction between water and liquid amalgams of sodium and potassium was chosen. These reactions have been shown to be photo-sensitive by Bhatnagar, Parshad and Mukherjee (This *Journal*, 1924, **1**, 263).

Experimental.

The polarising apparatus essentially consisted of two wooden chambers, one of which was fixed in position, while the other could be slided towards the fixed one or away from it on a base. The

base itself consisted of three plane pieces joined by means of two pairs of hinges, in such a way that the three parts could be folded on themselves. The top of the fixed chamber could be opened like the lid of a box, and from the near sides the boxes communicated with each other. The front of both the boxes was pierced by a hole 7 cm. in diameter to which two thin iron cylinders 14 cm. in length were attached. These cylinders served to lead the beams to the two reaction chambers, which were small wooden boxes covered all over with black paper, and the reaction vessels were placed inside these boxes to protect them from outside radiations. At the back of the fixed chamber was attached firmly an electric bulb. A hole was bored through the back of the movable box so that light could enter through it. Twenty-one glass plates were set in frame placed in the box. This frame could be rotated and the plates could be fixed at the desired angle. The two boxes could be brought near or taken apart without affecting the angle at which the plates were once arranged. When not in use the boxes were moved apart to their farthest ends and the base was folded, so that the whole thing could be converted into a big box.



A Fixed box. *G Glass plates.* *C Absorption Cell.*
B Movable box. *P Reflecting plates.* *V Reaction Vessels.*

Fig. 1.

The various parts of the apparatus in Fig. 1 are self-explanatory. Some plates were placed in the fixed box to equalise the intensities of the two beams so got. Thin plates of ground glass were placed in the path of the rays to make the beams homogeneous in intensity.

Two cells full of alum solution were interposed in the path of the beams to absorb the heat rays. The intensities of the beams were equalised by a sensitive thermopile and Broca galvanometer.

It was noted by means of a sensitive thermometer that the temperatures of the two beams were taken to see if a particular wavelength was missing in any of them.

Source of Light.—Ordinary 220 volts electric bulbs of 500 to 2000 c.p. were used according to the requirements of the experiment.

Polarisation.—The percentage polarisation of light depends upon the number of glass plates used and the angle at which the incident rays fall upon them.

The method used in measuring the percentage polarisation consisted in compensating the polarisation by means of one or more inclined glass plates.

Seven glass plates were placed between the polarised source of light and the Savart plate with its analysing nicol.

The Savart plate consists of a plane parallel plate cut from a quartz crystal at an angle of 45° to the optic axis. The plate is then sectioned parallel to the plane surface ; one half is rotated through 90° relative to the other and the two are cemented together.

" The glass plates are rotated until the Savart fringes disappear, *i.e.*, until the polarisation produced by transmission through the oblique plates exactly compensates the opposite polarisation originally present in the source. The angle θ through which the plates have been turned is read (*cf.* "Physical Optics" by R. W. Wood, pp. 298-299).

If the angle of incidence upon the inclined plate is θ and the refractive index of glass is μ, we can calculate ϕ, the angle of refraction from

$$\frac{\sin \theta}{\sin \phi} = \mu \text{ (refractive index)."}$$

Brewster found that the index of refraction was the tangent of the angle of maximum polarisation, which in the case of glass is 57·5°.

"From the theory of reflection we have for the ratio of the amplitude of the vibration perpendicular to the plane of incidence to that in the plane, for transmission through the two surfaces of a plate

$$\cos^2(\theta-\phi)$$

$\therefore$ the intensity ratio will be the square of this, or

$$\cos^4(\theta-\phi)$$

If we have n plates the intensity ratio will be equal to $\cos^{4n}(\theta-\phi)$."

Suppose we get $\cos^4(\theta-\phi)=1/x$,

then percentage polarisation $=\frac{x-1}{x+1}\times 100$

In the experiment $\theta=60{\cdot}50$; percentage polarisation $=88{\cdot}3$.

The Chemicals:—The chemicals used were all Merck's extra pure quality.

For the first reactions, namely the reduction of mercuric chloride by ammonium oxalate, saturated solutions of $(NH_4)_2C_2O_4$ and $HgCl_2$ were prepared in distilled water and stored in coloured bottles. The strengths of $(NH_4)_2C_2O_4$ and $HgCl_2$ solutions were 28·5 and 38·6 g. per litre respectively. The progress of the reactions could be studied by (1) comparing the volume of CO_2 gas evolved during the exposure in the two gases, or (2) by estimating the amounts of mercurous chloride precipitated in the two similar samples exposed to the two beams. As for the first method the volume of CO_2 evolved by the source of light used was found to be too little to saturate the solutions and then to indicate changes of volumes in the two capillary tubes attached to the reaction vessels and consequently the second method was adopted.

Thirty c.c. of $HgCl_2$ solution were mixed with 30 c.c. of $(NH_4)_2C_2O_4$ solution in a coloured bottle, 1 c.c. of $2N$ $FeCl_3$ was added and the whole was shaken.

Twenty-five c.c. of this mixture were taken in each test tube which were exposed to the two beams. After a definite interval of time the exposure was stopped and the contents of both the test tubes were filtered in two Gooch crucibles having asbestos pulp as the filtering materials. The crucibles were previously washed, dried in steam oven and weighed. The precipitates were washed till free from chlorides. They were then dried in the steam oven

and weighed till the weights were constant. The amounts of precipitates formed during the exposure were thus estimated. Some of the results are given below:—

TABLE I.

Time of exposure.	Amount of precipitate in m. gms obtained by exposure to polarised light.	Amount of precipitate in m.gms. got by exposure to unpolarised light.	Difference.
4 hours.	2·7	2·7	...
5 ,,	2·9	3·0	−·1
7½ ,,	4·4	4·3	+·1
11 ,,	7·0	7·2	−·2
15 ,,	10·1	10·2	−·1
24 ,,	14·3	14·2	+·1

TABLE II.

Reaction vessels interchanged.

4½ hours.	2·8	2·7	+·1
7½ ,,	4·2	4·4	−·2
8 ,,	4·5	4·4	+·1
11 ,,	6·8	7·0	−·2
16 ,,	10·3	10·4	−·1
24 ,,	14·4	14·2	+·2

An examination of the tables above will show that the amounts of precipitates obtained in both the beams are equal in all these experiments within the limits of experimental error, showing that both the beams are equally active in accelerating this reaction.

Reaction No. II.—The photo-decomposition of H_2O_2 is accelerated by alkalis and NaOH was therefore used as catalyst. Twenty-five c.c. of a 10 vol. strength solution of H_2O_2 (Merck's) were mixed with 25 c.c. of distilled water in a coloured bottle, 5 c.c. of 5 *N* NaOH added and the whole was thoroughly shaken.

Twenty-five c.c. of this mixture were taken by means of a dry pipette in the two test tubes which were placed in the boxes covered

black. Just before exposure samples were drawn from the two and their permanganate values were determined by titrations. As the exposure proceeded samples were again drawn from time to time and titrated in the same way. The results obtained are embodied in the following tables:—

TABLE III.

	Polarised beam.		*Unpolarised beam.*	
Time of exposure from the start.	Vol. of $KMnO_4$ used for samples.	Decrease in permanganate value due to decomposition.	$KMnO_4$ used for corresponding samples.	Decrease in permanganate value due to decomposition.
...	15·0 c.c.	...	15·0 c.c.	...
1 hour.	12·7 ,,	2·3	12·8 ,,	2·2
1½ ,,	12·0 ,,	3·0	12·2 ,,	2·8
2½ ,,	11·3 ,,	3·7	11·4 ,,	3·6
4 ,,	10·5 ,,	4·4	10·8 ,,	4·2
5 ,,	10·2 ,,	4·8	10·2 ,,	4·8
6 ,,	9·8 ,,	5·2	9·9 ,,	...

TABLE IV.

The vessels interchanged.

...	14·4 c.c.	...	14·4 c.c.	...
1½ hours.	13·3 ,,	1·1	13·3 ,,	1·15
2½ ,,	12·4 ,,	2·0	12·4 ,,	2·05
5 ,,	11·55 ,,	2·85	11·6 ,,	2·85
6½ ,,	10·8 ,,	3·6	10·8 ,,	3·65
7½ ,,	10·15 ,,	4·25	10·2 ,,	4·25
8½ ,,	9·6 ,,	4·8	9·6 ,,	4·85

The figures in the columns No. 3 and 5 of the above tables are very nearly equal in all cases and as they correspond to the decomposition of HO_2 by the two beams respectively, it is evident that in this case also polarised and unpolarised beams of equal intensity accelerate the reaction to an equal extent.

Heterogeneous Systems.

Reaction No. III.—The liquid amalgams of sodium and potassium react with water to produce hydrogen and their hydroxide even in the dark, but the reaction proceeds very much more vigorously in light and the velocity of the reaction can be measured fairly easily and accurately (1) by measuring the amount of hydrogen evolved and (2) by titrating the alkalis produced against standard acid. Both the methods have been employed in this investigation.

The amalgams were prepared by the electrolytic method of Richards (*J. Am. Chem. Soc.*, 1922, **44**, 601).

The amalgam was then dried and transferred to the storing vessel which consisted of a big separating funnel fitted with a rubber cork. It was connected to a hydrogen generator through a soda-lime tower, and a sulphuric acid gas-washing bottle. The washing bottle also comunicated with another vessel meant for taking out the amalgam in a current of hydrogen. The whole apparatus was completely covered with black paper to prevent the amalgams from being exposed to light.

The polarising apparatus was so designed that the whole arrangement could be turned through a right angle so that the electric vector vibrated at right angles to the plane of incidence. The results of these investigations have appeared in *Science* (Oct. 14th, 1927) and the details are described in a paper shortly appearing in the *Zeit. Phys. Chem.*

It is found that the perpendicularly polarised light accelerates the reaction considerably more than heterogeneous light, while the reaction is considerably less in parallel polarised light as compared to ordinary light. These results are analogous to the effect of polarised radiations on the photo-electric effect of these amalgams.

Discussion of Results.

As far as the results of the present investigation go, the following conclusions may be drawn from the same:—

1. Photo-chemical reactions in homogeneous systems are not sensitive to the state of polarisation of light.

2. In photo-chemical reactions constituting heterogeneous systems the state of polarisation of the radiant energy may have a selective effect.

In connection with the selective effect of palarised light on sodium and potassium amalgam it is interesting to recall the remarkable discovery of Elster and Geitel (*Weid. Ann. Physik*, 1894, **52**, 540) namely that the number of electrons liberated from a liquid alloy of sodium when exposed to light is much greater when the electric vector vibrates in the plane of incidence. These observations of Elster and Geitel have been confirmed by various workers notably by Pringsheim and Pohl.

The velocity and number of the electrons produced by light would determine the rate of photo-chemical reactions. The experiments of Elster and Geitel and Pohl and Pringsheim have established that the number of electrons liberated from these amalgams is much greater when the electric vector of the polarised light is vibrating in the plane of incidence. Hence it is natural to expect that the reaction between the amalgams and water will become accelerated under these conditions. These experiments constitute the first direct example of chemical reactions sensitive to the state of polarisation of the reacting light—the experiments of Weigert and Zocher (*loc.cit.*) being indirectly indicative of the same effect.

It is interesting to note here that Zocher and Weigert could prepare an optically active substance by the action of circularly polarised light on colloidal systems only. There is a certain amount of close similarity between their conclusions and the bearing of them on the results obtained here. It is also interesting to recall the failure of Ghosh and Mukherjee (this *Journal*, 1925, **2**, 165) to obtain a selective effect of polarised light on the photo-bromination of tartaric acid in aqueous solution. As the reaction studied by them constitutes a homogeneous system, it falls in line with our observations and confirms our conclusions.

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Dyes Derived From 1:2:3-Quinolinetricarboxylic Acid.

By Jamuna Dutt Tewari and Sikhibhusan Dutt.

Acridic acid, which is 1:2-quinoline dicarboxylic acid, contains two carboxyl groups in *ortho* position to one another, and is therefore expected to yield dyestuffs on condensation with aromatic amino- and hydroxy-compounds just in the same way as phthalic acid or quinolinic acid (Ghosh, *J. Chem. Soc.*, 1919, **115**, 1102).

Acridic acid differs from quinolinic acid in the same way as phthalic acid differs from naphthalic acid that is, by the presence in the latter of a fused benzene nucleus. From the point of view of the theory of colour that has been advanced by one of the present authors (Dutt, *J. Chem. Soc.*, 1926, **129**, 1171; also *J. Indian Chem. Soc.*, 1927, **4**, 99) it would be interesting to prepare pyronine dyestuffs from acridic acid and directly compare the intensity of their colour with the corresponding dyes derived from quinolinic acid, since by that means the effect of the fused benzene nucleus is easily ascertained. The effect of the nitrogen atom included in a ring system on colour, which is the main object of this series of papers, is also thereby seen by comparing colours of the dyes derived from acridic acid with the corresponding dyes derived from naphthalic acid. Hence it can be easily seen that from the theoretical point of view dyes derived from acridic acid, if they could be prepared, would be of considerable importance.

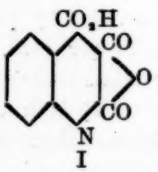
Unfortunately the only practicable method available for the preparation of acridic acid is by the oxidation of acridine by potassium permanganate. This method gives only about 10 per cent. yield of acridic acid, since in the oxidation reaction acridine is mainly transformed to pyridine tetracarboxylic acid, that is to say both the benzene nuclei in acridine are opened up by oxidation simultaneously, thereby considerably diminishing the yield of acridic acid. Besides this, the preparation of acridine itself in quantity is such a difficult affair, and the yield obtained is so bad, that for all intents and purposes acridic acid is practically an inaccessible material.

It was therefore thought that if some simple derivative of acridic acid could be fairly easily available, investigation could probably be

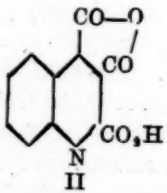
carried on with that substance instead of acridic acid itself. Amongst the higher homologues of acridine, 9-methyl-acridine can be prepared in good yield by the action of acetic acid and zinc chloride on diphenylamine at about 220° according to the method described by Fischer and Besthorn (*Ber.*, 1883, **16**, 74). This 9-methyl-acridine, on oxidation with potassium permanganate, gives an equally good yield of 1:2:3-quinoline-tricarboxylic acid, which is really 3-carboxy-acridic acid. The condensation of this acid with aromatic amino-, and hydroxy-compounds was therefore undertaken with the object of preparing dyestuffs which would be perfectly analogous in constitution to the corresponding dyes derived from acridic acid. Since a carboxyl in a dye molecule does not affect its colour to any appreciable extent as can be seen from the following table, it was therefore concluded that dyes derived from 3-carboxy-acridic acid would have practically the same colour as the corresponding dyes derived from acridic acid, and consequently would have the same theoretical importance.

Dyestuffs.	*Absorption maxima.*
Benzene-azo-phenol	4330
Benzene-azo-salicylic acid	4340
Benzene-azo-β-naphthol	4673
Benzene-azo-β-oxy-naphthoic acid	4680
Benzene-azo-pyrogallol	4430
Benzene-azo-gallic acid	4440
Benzene-azo-resorcinol	4470
Benzene-azo-β-resorcylic acid	4470

The only thing that remained to be settled was whether this 3-carboxyacridic acid would condense with aromatic amino-, and hydroxy-compounds in form I or II.

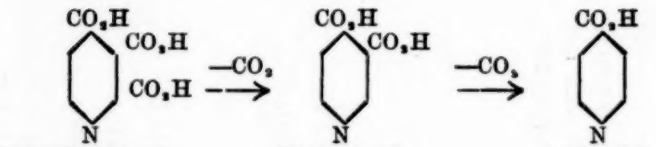


I



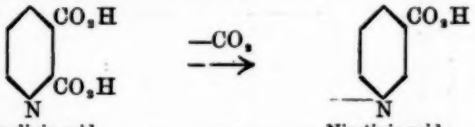
II

Form I was finally settled to be the form in which the condensations do actually occur by a study of the stability of the various pyridine carboxy-acids. Thus carbo-cinchomeronic acid on careful heating can be made to decompose by successive losses of carboxyl into cinchomeronic acid and finally into *iso*nicotinic acid.



Carbo-cinchomeronic acid. Cinchomeronic acid. *iso*-Nicotinic acid.

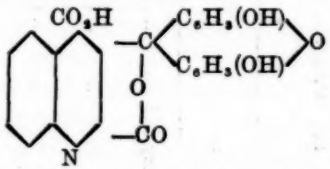
Similarly quinolinic acid on heating decomposes into nicotinic acid.



Quinolinic acid. Nicotinic acid.

Thus it is evident that the further away the carboxyl group is from the heterocyclic nitrogen atom the less reactive and consequently the more stable it is. Hence, since in the condensation products of 3-carboxy-acridic acid with aromatic amino- and hydroxy-compounds one carboxyl is found to remain intact, it must be the 3-carboxyl group, since it is the least reactive of the three carboxyl groups present in the above acid. Therefore it follows that in all the condensation products of 3-carboxyacridic acid, it must have reacted in form I.

3-Carboxy-acridic acid condenses with aromatic amino- and hydroxy-compounds with remarkable ease, even without the use of any condensing agents, though of course the use of small quantities of strong sulphuric acid or tin tetrachloride is advisable in order to get increased yields of the resulting dyestuffs. The structure of the resorcinol compound is given below:—



The structures of other compounds described are quite analogous to this. The following aromatic amino- and hydroxy-compounds have been condensed with 3-carboxy-acridic acid and the resultant dyestuffs isolated:—phenol, resorcinol, phloroglucinol, hydroxyquinol, *m*-diethylamidophenol and *m*-phenylenediamine. The absorption spectra of these compounds will be given in a comparative tabular form along with the last paper of the series. Since

these dyestuffs contain a quinoline nucleus, it is expected that they might have photosensitising properties also. Further investigation in that direction is now in progress.

Experimental.

The condensations of 3-carboxy-acridic acid with aromatic amino-, and hydroxy-compounds have been effected in the same manner as in the cases of β-phenyl-pyridine-dicarboxylic acid (Tewari and Dutt, this *Journal*, 1926, **3**, 161) and imidazole dicarboxylic acid (Tewari and Dutt, *Ibid*, 1927, **4**, 201). The results are summarised in the following table:—

Dyes derived from 1 :2 :3-Quinoline-tricarboxylic acid.

Name.	Appearance.	M. p.	Colour in alkali.	Colour of fluorescence.	Analysis (calc. % in brackets).
Phenol-3-carboxy-acridein ...	Pale yellow needles.	Above 280°	Pink	.....	C=69·3 (69·7); H= 3·4 (3·04).
Resorcinol ,, ...	Yellowish brown needles.	194°	Yellow	Yellow green	C=66·9 (67·4); H= 3·2 (3·04).
Phloroglucinol ,, ...	Orange needles	Above 280°	Orange red	.....	C=63·02 (62·7); H=2·4 (2·8).
Hydroxyquinol ,, ...	Brown needles	,, ,,	Deep pink	.....	C=63·1 (62·7); H= 2·7 (2·8).
m-Diethylamidophenol ,, ...	Pink needles	220°	Violet red (in acids).	Brown	N=7·4 (7·9).
m-Phenylenediamine ,, ...	Dark brown	Above 280°	Yellow brown (in acids).	Green	N=12·9 (13·2).

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Oil from *Pinus Gerardiana*— Chilgoza Oil. Part I.

By S. D. Hardikar.

Chilgoza is the fruit of *Pinus Gerardiana*, Wall. It is a moderately sized, ever-green tree belonging to the natural order *Conifer,æ* and is indigenous in the dry interior valleys of North-Western Himalaya, generally between 6,000—10,000 ft. from Kunawar westwards and in the territory of Garwhal. This tree is also grown in Afganistan and Persia. In Persia, the tree is called Sus, and in Afganistan it is termed as *Chil* and *Zan-ghozeh*, and hence the seed is generally known in India by the name of *Chilgoza*.

The chief product of this tree is the almond-like seed contained in the cones. The cones ripen in October, are plucked before they open, and heated to make the scales expand. The seed—the Chilgoza—is irregularly cylindrical about 1 inch in length. The shell is fairly stiff, and can be easily removed from the kernel. The kernels have a very thin upper covering, and are edible.

In Ayurvedic system of medicine, the seeds are considered as an anodyne, stimulant, and are also useful in chronic rheumatic affections. The oil extracted from the seeds is highly esteemed for its stimulating and healing powers when applied as adressing to wounds, ulcers, etc., and is also recommended to be employed as an external application in the diseases of the head. Since no work appears to have been done on the composition of the oil, the author has, therefore, undertaken a detailed chemical study of the seed as well as its oil.

Analysis of the Kernels from the Seed.

The weight of 100 seeds is on an average 30·4 gm. The kernel forms about 67·5 per cent of the seed, the husk on an average being 32·5 per cent. The kernels contain about 50·0 per cent. of the oil,

while the same calculated on the whole seed as such comes to about 33·7 per cent of the oil. The yield of the oil on pressing was found to be only 34·0 per cent.

Table I gives the analysis of the kernels.

TABLE I.

	Observers.	
	Author.	Church.*
Water	7·51 %	8·7 %
Proteins	15·87 %	13·6 %
Fat	49·91 %	51·3 %
Fibre	2·22 %	0·9 %
Ash	2·88 %	3·0 %
Carbohydrates	21·61 %	22·5 %
Food units	186	...
Nutrient ratio	1 : 8·6	...

Analytical Constants of the Oil.

The oil used for examination was obtained by pressing the crushed seeds in a juice extractor made of zinc. The oil is clear, and is of a pale yellowish colour. Grimme (*Agri. Ledger*, 1911-12, No. 5, p. 167) has also determined a few constants of the oil, and the values are given in Table II together with those obtained for the pressed oil examined in our laboratory.

TABLE II.

	Observers.	
	Author.	Grimme.
Specific gravity	0·9144 at 32°C	0·9307 at 15°C
Refractive index	1·4709 at 32°C	...
Acid value	3·87	1·6
Saponification value ...	192·4	191·3
Acetyl value	4·07	...
Iodine value	121·3 (Hubl's)	118·0 (Wij's)
Unsaponifiable matter ...	0·50	...
Iodine value of the above ...	68·4	...
Reichert-Meissl value ...	0·33	...
Hehner value (fatty acids) ...	95·01	91·46

Table III gives the analytical constants of the fatty acids separated from the oil.

* *Pharmacographia Indica*, 1893, 3, 380.

TABLE III.

	Observers.	
	Author.	Grimme.
Specific gravity	0·8952 at 30°C.	...
Index of refraction	1·4622 at 30°C.	...
Iodine value	127·7 (Wij's)	125·0 (Wij's)
Neutralisation value	200·9	196·7
Mean molecular weight	280·2	285·2

Composition of the Oil.

The saturated and the unsaturated acids in the fatty acid portion were estimated by (*i*) the lead-salt-ether method, and (*ii*) by Twitchell's lead alcohol method (*J. Ind. Eng. Chem.*, 1921, **13**, 806). In the experiment with the latter method 10 gm. of the oil were saponified with alcoholic potash, the dry potassium soap extracted with ether to remove unsaponifiable matter, and then decomposed with hydrochloric acid. From the portion of the fatty acids thus obtained 8 gm. were dissolved in 200 c.c. of 95% alcohol, heated to boiling, and to this was added a boiling solution containing 5 gm. of lead acetate in 100 c.c. of 95% alcohol. The mixture was kept at room temperature overnight. The precipitate was then washed with cold 95% alcohol until the washings were free from lead. The precipitated lead salts were then redissolved in 100 c.c. of boiling 95% alcohol and 0·5 gm. of acetic acid, and the solution cooled overnight. The precipitate was then removed, washed with 95% alcohol, washed from the filter with ether, and decomposed with dilute nitric acid. The ethereal solution containing the solid fatty acids was then washed with distilled water in a 100 c.c. seperator until the washings were no longer acid to methyl orange. The ether was then evaporated, the residue dried and weighed.

Table IV gives the percentages of the saturated and the unsaturated acids as estimated by the two methods.

TABLE IV.

	Percentage of saturated acids.	Percentage of unsaturated acids.
Lead salt-ether method ...	6·57	93·43
Twitchell's method ...	4·92	95·08

The iodine value of the portion of saturated acids obtained by method (*i*) was found to be 49·4. This indicates the presence of a

little unsaturated acid being left in the sample. The portion of the saturated acids prepared by the Twitchell's method was pure white, its m.p. being 53°·5.

Unsaturated Acids.

The unsaturated acids were examined by means of their bromine additive products as recommended by Jamieson and Baughman (*J. Am. Chem. Soc.*, 1920, **42**, 1198).

The unsaturated acids for this work were prepared according to the method of Eibner and Muggenthalor (Lewkowitsch, " Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th edition, Vol. I, p. 573) according to which 2 gm. of the unsaturated acids were dissolved in 50 c. c. of dry ether, cooled in ice to 0°; bromine was then slowly added, and the mixture allowed to stand for two hours at about —10°. At this stage, no precipitate insoluble in ether was obtained, which indicates that no linolenic acid is present in the unsaturated portion of the acids (the hexabromo-derivative of linolenic acid is insoluble in ether). The excess of bromine was then removed from the ethereal solution by washing it with an aqueous solution of sodium thiosulphate in a seperator. All traces of water were then removed from the washed ethereal solution by means of anhydrous sodium sulphate, and the ether was removed by distillation. The residue was then taken up with 100 c. c. of petroleum ether (b. p. 60-80°), and cooled in an ice-box for overnight. A precipitate of linolic tetrabromide was obtained.

From the above, it is clear that in the portion of the unsaturated acids, linolenic acid is absent, while linolic and oleic acids are present. As we were short of bromine in our laboratory to repeat the above quantitatively for ascertaining the percentages of the tetrabromide and the dibromide, the percentages of the linolic and the oleic acids in the unsaturated portion were arrived at from an estimation of the iodine value of the unsaturated acids. The iodine value of the above was estimated both by Hubl's as well as Wij's method. Both the methods gave nearly the same value, the mean being 129·2.

For the purpose of calculating the percentages of linolic and oleic acids from the iodine value of the unsaturated portion, the following equations have been used.

$$x+y=100.$$

$$90{\cdot}07x+181{\cdot}42y=100\ \text{I}.$$

where x=per cent. of oleic acid in the unsaturated portion;
y=per cent. of linolic acid in the unsaturated portion;
and I=Iodine value of the unsaturated portion.

Table V gives the percentages of oleic and linolic acids calculated from the above equations.

TABLE V.

	Percentage in the unsaturated portion.	Percentage in the original oil.
Oleic acid	57·2	54·4
Linolic acid	42·8	40·7

Saturated Acids.

The saturated acids for the purpose of the examination were prepared according to Twitchell's method. The percentage of the saturated acid portion in the oil being only about five, more than a kilogram of the oil had to be treated for the preparation of the saturated acids in order to get a sufficient quantity of the material for further analytical work. Thirty-five gm. of saturated acids were obtained from one kg. of the oil.

The saturated acids (35 g.) were converted into methyl esters by the Fischer-Speier process by boiling for four hours with five times its weight of methyl alcohol containing 4 per cent. of dry hydrogen chloride, pouring into water, and then extracting with ether.

Summary and Conclusions.

The oil is a non-volatile fixed oil belonging to the class of semi-drying oils. Nearly 95 per cent. of the oil consists of glycerides of unsaturated fatty acids, namely oleic and linolic, the remaining 5 per cent. being the glycerides of saturated fatty acids. Further investigation on the saturated acid portion is in progress.

In conclusion, I wish to express my gratitude to Mr. Bodhraj Sobti, M.Sc. for the kind interest he took in this investigation.

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On a new Series of Double Sulphates of the Copper-Magnesium Group and the Sulphonium Bases. Part II.

By Prafulla Chandra Ray and Nirmalendunath Ray.

It has already been shown that sulphates of the copper-magnesium group yield with the alkyl sulphonium sulphates double salts which in the case of the ethyl derivative conform generally to the formula $M''SO_4 \cdot (R_3S)_2SO_4, 10H_2O$ (*i*) where M″=a metal of the vitriolic series and R=Et.

Exceptions were found in the cases of magnesium and manganese, which yielded salts of the type $2M'' SO_4 \cdot (R_3S)_2 SO_4, 11 H_2O$ (*ii*) (*J. Indian Chem. Soc.*, 1927, **4**, 37).

In the present communication the action of trimethyl sulphonium sulphate upon the above vitriolic sulphates has been studied. It has been found that double salts of the first type are almost invariably formed, the only difference being that they are octahydrated instead of being deca-hydrated. Nickel and cobalt seem in the first instance to present certain anomalies. The first crops of these salts conform to the second type or to a mixture of the two types; but the subsequent crops are invariably of the first type.

The properties of these double sulphates are very similar to those obtained from thriethyl sulphonium sulphate and the vitriolic sulphates; the only difference being in the degree of stability, deliquescent character and crystalline shape of the substances. For whilst the triethyl sulphonium double sulphates (*loc. cit.*) crystallise in needles, the corresponding trimethyl compounds crystallise in plates. The latter are much more stable and less hygroscopic than the former. The trimethyl sulphonium double sulphates are all readily soluble in water and when the concentrated aqueous solutions are treated with alcohol, hepta-hydrated double salts are precipitated. In the case of cobalt, however, the salt is hexahydrated while the nickel salt under similar circumstances remain unchanged as to the degree of hydration. In this respect these double salts show a marked contrast to the triethyl sulphonium double sulphates (*loc. cit.*). This difference of behaviour may be ascribed to the fact that while the triethyl sulphonium sulphate is extremely soluble in alcohol, the corresponding trimethyl compound is only sparingly so.

Experimental.

General Method of Preparation.—The component inorganic and organic sulphates respectively were mixed in the proportion of 1:2 as it was found by previous experience that if they are mixed in equimolecular proportions, at first only the vitriolic sulphates crystallise out.* The solution was concentrated at first in a vacuum over sulphuric acid and finally left to spontaneous evaporation. The crystals obtained were drained free from the mother-liquor and dried between folds of filter paper. These were then powdered and completely dried in air before analysis.

Ferrous-trimethyl-sulphonium Sulphate.—The crystalline double salt was coloured like ferrous ammonium sulphate. (Found: Fe, 10·30, 10·34; C, 13·96; H, 6·18. $FeSO_4 \cdot \{(CH_3)_3S\}_2SO_4$, 8 H_2O requires Fe, 10·26; C, 13·18; H, 6·23 per cent.).

On treating the concentrated aqueous solution with alcohol a white crystalline compound was precipitated. (Found: Fe, 10·65. $FeSO_4\{(CH_3)_3S\}_2SO_4$, 7 H_2O requires Fe, 10·67 per cent.).

Zinc-trimethyl-sulphonium sulphate was obtained as a white crystalline substance. (Found: Zn, 11·65; SO_4, 36·08. $ZnSO_4 \cdot \{(CH_3)_3S\}_2SO_4$, 8 H_2O requires Zn, 11·71; SO_4, 34·59 per cent.).

On precipitation of a concentrated solution of the salt with alcohol, a finely divided white crystalline compound was obtained. (Found: Zn, 12·14. $ZnSO_4\{(CH_3)_3S\}_2SO_4$, 7 H_2O requires Zn, 12·15 per cent.).

Cadmium-trimethyl-sulphonium sulphate was a white crystalline compound. (Found: Cd, 18·91; SO_4, 32·81. $CdSO_4\{(CH_3)_3S\}_2SO_4$, 8 H O requires Cd, 18·64; SO_4, 31·86 per cent.).

Treatment with alcohol of a concentrated aqueous solution of this substance yielded a white crystalline precipitate. (Found: Cd, 19·10; SO_4, 33·24. $\{(CH_3)_3S\}_2SO_4$, 7H_2O requires Cd, 19·04; SO_4, 32·82 per cent.).

Magnesium-trimethyl-sulphonium sulphate was obtained as a transparent crystalline substance. (Found: Mg, 4·76; SO_4, 37·33; C, 12·85; H, 6·73. $MgSO_4\{(CH_3)_3S\}_2SO_4$, 8$H_2O$ requires Mg, 4·72; SO_4, 37·31; C, 13·98; H, 6·60 per cent.).

* It has subsequently been found that in the present case by using equimolecular proportions of the component sulphates, the double salt may also be formed.

On adding alcohol to a concentrated aqueous solution of the substance a white crystalline compound was precipitated. (Found: Mg, 4·92. $MgSO_4\{(CH_3)_2S\}_2SO_4, 7H_2O$ requires Mg, 4·89 per cent.).

Copper-trimethyl-sulphonium sulphate was obtained as a blue crystalline compound. (Found: Cu, 11·53. $CuSO_4\{(CH_3)_2S\}_2SO_4, 8H_2O$ requires Cu, 11·48 per cent.).

Addition of alcohol to a concentrated aqueous solution of the substance caused a blue crystalline compound to be precipitated. (Found: Cu, 11·87. $CuSO_4\{(CH_3)_2S\}_2SO_4, 7H_2O$ requires Cu, 11·86 per cent.).

Manganese trimethyl sulphonium Sulphate.—The double salt was coloured slightly pink. (Found: Mn, 10·27, 10·25. $MnSO_4\{(CH_3)_2S\}_2SO_4, 8H_2O$ requires Mn, 10·09 per cent.).

Precipitation with alcohol from a concentrated aqueous solution of the substance yielded a slightly pink coloured (nearly white) crystalline compound. (Found: Mn, 10·55. $MnSO_4\{(CH_3)_2S\}_2SO_4, 7H_2O$ requires Mn, 10·42 per cent.).

Nickel trimethyl sulphonium sulphate was obtained as a green crystalline compound. In the first crop the ratio of the number of nickel atoms to the number of SO_4 radicals was 2:3 as described in the previous paper (*loc. cit.*). But the second and the subsequent crops on analysis were found to be of the usual type. (Found: Ni, 10·40, 10·58; C, 12·59; H, 6·19. $NiSO_4\{(CH_3)_2S\}_2SO_4, 9H_2O$ requires Ni, 10·69; C, 13·11; H, 6·19 per cent.).

Cobalt trimethyl sulphouium Sulphate.—This double salt was coloured like cobalt sulphate crystals. The first crop on analysis was found to be of indefinite composition as the metal did not exist in any simple ratio with the SO_4 radical and hence by analogy with the nickel compound it was evident that the substance was made up of a mixture of the two types (*i*) and (*ii*). The second crop and the successive crops were of the general type. (Found: Co, 11·19. $CoSO_4\{(CH_3)_2S\}_2SO_4, 8H_2O$ requires Co, 10·74 per cent.).

The substance obtained from a concentrated solution of it by precipitation with alcohol was also coloured like cobalt sulphate. (Found: Co, 11·53. $CoSO_4\{(CH_3)_2S\}_2SO_4, 6H_2O$ requires Co, 11·50 per cent.).

Water of Crystallisation of the Double Salts.—The number of water molecules has been determined by direct combustion. The number of hydrogen atoms in excess of that required by the organic component gives that present as water. Estimation of water by

simply heating cannot strictly be relied upon, since on heating even at 110°—115° the molecules of the double salt decompose, a portion of the organic component escaping along with some molecules of water. The double salts again exhibit various degrees of stability on heating to the same temperature. It has been found that in the case of the cadmium compound on heating to 115°, nearly seven molecules of water can be driven out along with traces of the organic component. (Found, dehydrated product: Cd, 24·00; C, 14·57; H, 4·77. $CdSO_4\{(CH_3)_2S\}_2\ SO_4,\ H_2O$ requires Cd, 23·40; C, 15·09; H, 4·19 per cent.).

The magnesium compound loses eight molecules of water on heating at 115°. (Found: loss in weight, 27·42. $MgSO_4\{(CH_3)_2S\}_2\ SO_4,\ 8H_2O$ requires 27·99 per cent. loss on complete dehydration. The dehydrated product on analysis gave C, 19·39; H, 5·63* per cent. $(MgSO_4\ \{(CH_3)_2S\}_2\ SO_4$ requires C, 19·40; H, 4·89 per cent.).

By heating the double salts to higher temperatures than described above, it was found that continuous loss of weight occurred, indicating decomposition, which was most conspicuous by the evolved smell of methyl sulphide.

Some of the physical properties of this series of compounds including their crystallography will form the subject of a subsequent communication.

In conclusion we avail ourselves of this opportunity to express our sincere thanks to Mr. K. C. Bose-Rây for his kind help in conducting some of the analyses.

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* Owing to the intense hygroscopic character of the dehydrated salt some moisture is absorbed during operation and thus hydrogen comes out too high.

Note.—In support of the formulae assigned to the salts it may be emphasised that successive crops of the same preparation always give identical analytical results and that the resemblance between all the members of the series points to their having the same degree of hydration.

Co-ordination and Atomic Structure.

By Priyadaranjan Ray.

The present position of the electronic theory of valency as developed by Kossel, Lewis and Langmuir and applied to simple compounds can be briefly summarised as follows:—

Each atom tends to assume the electronic configuration of the nearest inert gas in a chemical combination with other atoms either by transfer, acceptance or sharing of electrons. This exchange and sharing are confined to the electrons of the outermost layers. These electrons are therefore known as valency electrons. Each valency bond in the case of sharing is supposed to consist of a pair of electrons and is known as co-valence or homœpolar binding. The exchange of electrons gives rise to what is known as electro-valence or heteropolar binding.

This theory in its static form explains quite satisfactorily the valence-phenomena of many elementary atoms specially of the first two short periods, as manifested in their simple compounds. But when considered in the light of later developments regarding the distribution of electrons into groups and sub-groups as illustrated by the work of Bohr (*Nature*, 1923, **112**, 29) and specially by that of Smith (*Chem. and Ind.*, 1924, **43**, 323) and Stoner (*Phil. Mag.*, 1924, vi, **48**, 719) based on the investigations of optical and X-ray spectra of elements, certain difficulties are encountered in the application of this theory to the non-polar compounds like those of carbon.

Following Stoner-Smith's scheme of electron distribution into various sub-groups in the case of carbon and nitrogen for instance—

		Number of electrons.			
Atomic Number.	...	K_{11}	L_{11}	L_{21}	L_{22}
6 C	...	2	2	2	...
7 N	...	2	2	2	1

we find that in compounds like CH_3Cl, CH_2Cl_2. $CHCl_3$, NH_2OH and many substituted ammonium salts different isomeric types

of molecules might arise due to the possibility of sharing of electrons by any individual atom from different orbital sub-groups in the L-level of carbon and nitrogen—the energy content of this particular atom differing with the position of the carbon or nitrogen electron with which it might share one of its own electrons. Such a differentiation, however small, would at least lend itself to detection by delicate optical methods. Samples of the same substance, chloroform for example, prepared by different methods might have been expected to exhibit this difference, which however is unknown. This may be explained either by assuming that all these substances are equilibrium mixtures of different types of molecules or during combination a redistribution of the electrons occurs which does not permit of any such differentiation. In $CHCl_3$ for instance, it may be assumed that the eight-shared electrons between carbon and the other combining atoms are rearranged into two groups of four each in the L-level of carbon, one from each such group entering into every covalent bond. The atoms or groups may then be pictured as arranged at the corners of a regular tetrahedron around the central carbon atom. So the atom returns to the original Bohr grouping for L-level. This latter is the more probable explanation.

The electronic theory of valency in its above simple form fails to account for the formation of the so-called co-ordination compounds by many elements of the transitional groups of Bohr's periodic system. Chromium, iron, cobalt, molybdenum, tungsten, rhodium, palladium, iridium and platinum are the elements specially characterised by this property.

Kossel (*Ann. Phys.*, 1916, **49**, 229) suggests that the formation of complex compounds is due to electrostatic attraction of the central nuclear ion for the surrounding atoms or radicles. According to his view the electro-affinities of ions are not completely saturated in their simple salts or compounds. The unsaturated residual affinity of the central atom then attracts molecules or radicles with atoms having similar residual affinities of an opposite character—the strength of the attraction varying with the charge on the central atom and its radius.

Briggs (*Phil. Mag.*, 1926, *ii*, **11**, 1026) like Kossel in a very ingenious and interesting theory termed as the theory of duplex affinity regards the electrostatic attraction as the cause of complex-formation. And like Werner he introduces the idea of primary and secondary affinities. But his primary and secondary affinities are of different

sign as opposed to those of Werner. According to Briggs a potassium atom for example, which has a tendency to give up an electron and thus change into a positive ion has got a primary positive affinity. But the potassium ion on the other hand, because of the very nature of its being positively charged has a tendency to attract negative electrons or ions and has thus acquired a secondary negative affinity. Similarly chlorine is an element with a primary negative affinity but secondary positive affinity so far as the mutual relationships of the two elements are concerned. Formation of complex compounds is then attributed by him to the exercise of these unsaturated secondary affinities. In a simple compound like carbon tetrachloride, where both the primary and secondary affinities of the combining atoms are completely saturated, the substance becomes non-polar and fails to give rise to any complex formation. Briggs has succeeded in explaining satisfactorily many important properties and characteristics of complex compounds by this simple theory. Though this theory supplies a very plausible explanation of the hidden force that gives rise to complex formation, that is not, however, the only factor that governs such combinations. Had it been so almost all positive elements specially those more electropositive than cobalt and of about the same atomic volume—elements like Be, Mg, Al, Zn, Mn, Cd and Tl should give at least as stable complex compounds as cobalt. This is however not the fact. Similar objections can be raised against Kossel's view as well.

A very important contribution towards elucidation of the structure of co-ordination compounds has been made by Sidgwick (*J. Chem. Soc.*, 1923, **123**, 725), according to whom in the formation of a co-ordination compound the central atom tends to assume the external electronic configuration of the next higher inert gas, the co-ordinated atoms, groups or molecules being held by co-valency to the central nuclear atom. Butler (*Trans. Farad. Soc.*, 1925, **21**, 349) however does not recognize Sidgwick's interpretation and assumes that the electrons contributed by the co-ordinated units form a distinct group round the central ion. That is, the co-ordination electrons enter the main quantum group next to that represented in the central ion. There is however, no physical conception behind such an assumption and it seems to be more or less speculative.

Sidgwick's view has, however, been supported by Lowry (*Discussion, Farad. Soc.*, "Electronic theory of valency," 1923; *Chem.*

and Ind., 1923, **42**, 316), Fowler (*Discussion, Farad. Soc.*, "Electronic theory of valency," 1923) and Spiers (*Chem. and Ind.*, 1923, **42**, 534) and its importance has been revealed by Welo and Baudisch (*Nature*, 1925, **116**, 606). Welo and Baudisch have shown that the complex compounds whose "effective atomic number" is equal to that of the next higher inert gas exhibit diamagnetism due to the formation of closed configuration resembling that of the latter. On the other hand those complexes whose "effective atomic number" is not equal to that of the following inert gas show paramagnetism. Bose (*Zeit. Phys.*, 1925, **35**, 213, 219) has further assumed that their magnetic moment in Bohr's magneton number are mostly proportional to the difference between their "effective atomic number" and the atomic number of the next higher inert gas. This furnishes a strong evidence in support of Sidgwick's interpretation of the structure of complex compounds. There are however some exceptions specially in the case of less perfect complexes.

Bose (*loc. cit.*) has proposed a scheme of electron distribution among various subgroups of the main quantum groups for the elements of the first transitional group as well as for their ions, which, according to him satisfactorily explains their magnetic moment. From this he has also developed a scheme of electron-distribution for the complex compounds of Cr, Fe, Co, Ni and Cu. But this scheme cannot explain the physical and chemical properties of the complex compounds in all cases as he introduces a differentiation in the co-ordinated units by placing the shared electron pairs among different subgroups of M- and N-quantum groups. But as is well known Werner in the case of perfect complexes has definitely proved the equivalence of the six co-ordinated units which occupy the corners of a regular octahedron and exhibit well-defined types of isomerism. This cannot be possible in the case of such a differentiation of the co-ordinated units.

Another proposal for the electronic configuration of the complex compounds of the first transitional elements has been made by Cabrera (*J. Phys. Radium*, 1925, **6**, 276) from a consideration of their magnetic moment. This view has been favourably reviewed by Jackson (*Phil. Mag.*, 1926, **2**, 87). Cabrera's scheme of representation may be regarded as more or less identical with that of Butler, only with this difference that the significance of Sidgwick's rule has not been ignored. According to this scheme a group of 12 electrons divided into 2 subgroups of 6 each representing the 6 co-ordination units in

the case of sixfold co-ordination compounds or a group of 8 electrons divided into two sub-groups of 4 each for the fourfold co-ordination, are arranged in a separate group after the M- quantum group.

This group of 12 electrons as a whole is supposed to possess no magnetic moment. Cabrera's arrangement does not give an external electronic configuration of the next higher inert gas to the co-ordination complexes and thus deviates from the uniform plan of atom-building process. Further he attributes the same configuration to both Mn^{++} and Fe^{+++} ions but does not explain why ferric iron forms well-defined complexes whereas the corresponding manganous compounds are extremely unstable. The arrangement also suffers from the same defect as was noticed in the case of Butler's proposal having no definite physical conception behind it. Cabrera seems to attach more importance to the total number of electrons than to their configuration.

Before attempting to give any definite electronic configuration to the co-ordination complexes we must thoroughly take into account their physical and chemical properties. From a consideration of these properties it will be found that the complex compounds as a rule can be divided into two main classes depending on their complexity. These can be termed *strong or perfect* and *weak or imperfect* complexes. To the former belong almost all sixfold complexes of cobaltic cobalt, some sixfold complexes of ferrous and ferric iron, all sixfold and fourfold complexes of platinum and the sixfold complexes of chromic chromium, tervalent rhodium, tri- and tetra-valent iridium and a few ruthenium compounds. These are distinguished by their extraordinary complexity and characteristic chemical properties. The rest of the so-called complex compounds coming under the latter head form as it were a transition between true complexes and the double or associated compounds. To the former, therefore, we can very reasonably ascribe a more or less inert gas configuration in accordance with Sidgwick's interpretation.

First of all we must consider the electronic arrangement in the transitional elements and in their simple ions. No definite or fixed arrangement can be regarded here as satisfactory and sufficient to explain all their physical and chemical properties. This is the reason why a number of different schemes of grouping have been proposed by different investigators. Besides Smith-Stoner's original scheme, others like those of Swinne (*Zeit. Elektrochem.*, 1925, **31**, 417), Bose (*loc. cit.*), Samuel and Markowicz (*Zeit. Phys.*, 1926, **38**,

22), Lessheim and Samuel (*Zeit. Phys.*, 1926, **40**, 220) for the transitional elements of the first group may be mentioned in this connection. In fact it may be assumed with some reason that in these elements or in their ions the electrons in the M_3-level are rather mobile and prone to ready rearrangement between the two sub-groups under external chemical influences. In the case of certain elementary ions it may further be assumed that there is an equilibrium mixture of two or more types with different arrangement of electrons in the M_3 sub-groups, or in other words, such ions may be regarded after Swinne as a mixture of "electronic isomers" in equilibrium. In fact the magnetic moment curve for the ions of the transitional elements of the first group shows some pronounced irregularities in the region corresponding to iron and cobalt ions. Following electron-distribution for these elements is in better accord with their chemical behaviour than any other previously proposed and it has the further advantage of explaining the formation of co-ordination complexes without much difficulty (Table I). As for the magnetic moment of the ions, we can under the present circumstances simply hold after Ladenburg (*Naturwissenschaften*, 1920 **8**, 6) that it is only the incompleted groups that contribute to this effect. Following simple assumptions are made in formulating this scheme. An odd electron in the M_{3_2} sub-group is very mobile specially at the commencement of the formation of the group and readily acts as a valency electron whereas every two electrons tend to produce a more or less stable coupling. The stability of a group on the whole increases with the number of electrons in it.

Reference may be made in this connection to Hund's (*Zeit. Phys.*, 1925, **33**, 362) distribution of electrons based upon an analysis of the complicated spectra of these elements. Hund does not distinguish between the M_{3_2} and M_{3_3} sub-groups, *i.e.*, he does not split up the M_3 electrons into two sub-levels. But as such a sub-division is necessary from the chemical standpoint, it is quite reasonable to assume that the M_3 group may split up into M_{3_2} and M_{3_3} in more than one way during chemical union depending upon external conditions and the mode of combination. We may thus regard the atom as passing into an active phase during chemical union. In Table I we stick to Hund's (*loc. cit.*) distribution for the neutral atoms. In the case of cobaltic ion it will be noticed that it behaves as a mixture of two electronic isomers which thus accounts for its anomalous magnetic behaviour.

TABLE I.

Atoms and ions.	Electron number.	Number of electrons in different groups.				Bohr's magneton number.
		K_{11} to M_{22}	M_{23}	M_{33}	N_{11}	
Cr	24	18	... 4		2	
Cr^{++}	22	18	3 ...	1		4
Cr^{+++}	21	18	3 ...			3
Mn	25	18	... 5		2	
Mn^{++}	23	18	1 ...	4		5
Fe	26	18	... 6		2	
Fe^{++}	24	18	3 ...	3		4
Fe^{+++}	23	18	3 ...	2		5
Co	27	18	... 7		2	
Co^{++}	25	18	3 ...	4		4
Co^{+++}	24	18	(*a*) 4 ...	2		2·5
			(*b*) 3 ...	3		(Weber, *Ann. Phys.*, 1911, 36, 624)
Ni	28	18	... 8		2	
Ni^{++}	26	18	4 ...	4		2
Cu	29	18	... 9		2	
Cu^{+}	28	18	4 ...	6		Diamagnetic.
Cu^{++}	27	18	4 ...	5		1

We shall now proceed to discuss the formation of co-ordination complexes by the ions with electronic configurations as described in Table I. In the first place, we shall deal only with the strong sixfold complexes. Their electronic configurations are given in Table II.

TABLE II.

Name of the Complex.	Number of electrons in various groups.					Number of Bohr's magneton.
	K_{11} to M_{22}	M_{23}	M_{33}	N_{11}	N_{23}	
Cr^{+++} complex	18	3	6		6	3
Fe^{++} complex	18	4	6	2	6	Diamagnetic.
Fe^{+++} complex	18	4	6	1	6	1
Co^{+++} complex	18	4	6	2	6	Diamagnetic.

In this scheme it will be noticed that the 12 electrons supplied by the six co-ordinating units arrange themselves in 6 pairs of orbits belonging to the M_{33} sub-group and N_3 group. It is assumed here that the N_3 group had no occasion to split up into two sub-groups N_{31} and N_{33} as it had previously no electron of its own supplied by the central ion. Every one electronic orbit of M_{33} is thus coupled with one of N_3 to form a pair of shared orbits for each co-ordinating unit of the sixfold complexes. This maintains the equivalence of the six units and does not give rise to any differentiation whatsoever. They are thus symmetrically arranged around the corners of a regular octahedron as required by Werner's theory. The configuration thus produced resembles closely that of the next inert gas krypton specially in the case of diamagnetic cobaltic and ferrous complexes, excepting that the electrons of the M_{33} and N_3 groups are not in the sole possession of the central atom but equally shared between it and the associating units. Ionizable atoms thus bound, as for instance chlorine in chloropentammine complexes can not easily come out as ions as it shares electrons from a now comparatively inner level like M_{33}. This is specially noticeable in the case of cobaltic and ferrous complexes where N_{11} group is completely filled up, which further stabilizes the M_{33} subgroup. The electrons in N_{11} group cannot further act as valency electrons because of a shielding layer of N_3 electrons.

Now if we analyse the mechanism of formation and the stability of these complexes it will be observed that manganese complexes of the perfect type are either incapable of formation or even if formed will be extremely unstable. Taking the case of cobalt first, we find from the table that the cobaltic ion is assumed to be an equilibrium mixture of two electronic isomers (a) and (b). One (a) has the electron distribution of 4 in M_{33} and 2 in M_{32}. This is the configuration most active in the complex formation. The other arrangement (b) with 3 electrons in M_{33} and 3 in M_{32} represents its ordinary chemical behaviour and its instability. Free cobaltic ion is known to change readily into the cobaltous one. Now in the (a) phase of the cobaltic ion the M_{33} group is complete and there are only 2 electrons in M_{32}. Under the influence of strongly polar molecules, groups or ions, these are pushed out to the now vacant N_{11} level thus completing the latter and at the same time both the M_{32} and N_3 levels are filled up by the sharing of electrons with the co-ordinating units. On the other hand.

cobaltous ion is incapable of forming such strong sixfold complexes. This is evident from its electron distribution, In this there are 3 electrons in the M_{3_2} and 4 in the M_{3_3} subgroups. Now 4 electrons in the M_{3_3} level form a comparatively stable grouping. Besides there will be no accommodation for the six shared electrons in it even if two of the four electrons of the M_{3_3} level be shifted to N_{1_1} and one to M_{3_2} level — there being still one electron left in M_{3_3}. Only under the influence of powerfully polarised co-ordinating ions like -CN this last electron can be forced out of M_{3_3} to a distant outer level to form a compound like potassium cobalto-cyanide, but the latter becomes thereby extremely unstable and this lone electron will readily act as a valency electron leading to the oxidation of the cobaltocyanide to cobalticyanide. This is what actually happens. Potassium cobaltocyanide as is well known is oxidized even by water with evolution of hydrogen gas.

Turning to the iron complexes it will be noticed that the configuration of the ferrous complex indicates a perfectly stable one resembling that of the next inert gas krypton. But the formation of ferrous complex can not take place easily. Since there is a group of 3 electrons in M_{3_2} level of ferrous iron, of which only two can be knocked out to N_{1_1} level, there will still remain one. This can only find place in M_{3_4} level. But only the action of strongly co-ordinating polar substances like α α-dipyridyl molecules and cyanogen ions can compel this last electron to move back to M_{3_2} specially as the charge on the ferrous ion is comparatively low amounting to two units only. Hence we are acquainted with compounds like potassium ferrocyanide but with no positive ammoniacal complexes like hexammine, pentammine or tetrammine salts. Ferric complexes from the very nature of their configuration will be unstable having one lone electron in the N_{1_1} level which tends to stabilize itself readily coupling with a second electron. $\alpha\alpha$-dipyridyl ferric complex, as is well-known, readily passes into the ferrous complex and potassium ferricyanide for this reason acts as a powerful oxidizing agent. On the other hand we know that simple ferrous ion readily passes into the ferric state owing to the former's having one odd electron in the M_3 level.

Manganese ion having a fairly stable grouping of 4 electrons in the M_{3_3} level fails to produce any stable complex compound. And we are aware of only very unstable mangano-and mangani-cyanides. It appears that in any sub-group the stability increases with the

number of electrons as it becomes gradually filled up and an odd electron has a tendency to act like a valency electron or form a close couple with another.

Chromium complexes are more readily formed as the M_{33} level being vacant is fully available for sharing. The complexes are therefore fairly stable on account of their more or less symmetrical external configuration. They are however much less stable than the corresponding cobalt compounds due to their N_{11} level remaining unoccupied. Chromous ion having a low valency cannot give rise to a stable complex specially as the odd electron in M_{33} would add to the instability.

Now we shall take up the cases of perfect sixfold complexes of molybdenum, rhodium, iridium and platinum. The electron distribution in their atoms, ions and corresponding complexes are given in Table III. As before we follow Hund's scheme for the neutral atoms.

TABLE III.

Name.	Number of electrons in various groups.					Bohr's magneton number.
	K_{11} to N_{22}	N_{23}	N_{33}	O_{11}	O_{23}	
42 Mo	36	... 4	...	2	...	
Mo^{+++}	36	3	...	...	...	
Mo^{+++} complex	36	3	6	...	6	3 (Rây and Bhar, *private communication*).
45 Rh	36	... 7	...	2	...	
Rh^{+++}	36	4	2	...		
Rh^{+++} complex	36	4	6	2	6	Diamagnetic.

Table III continued.

Name.	Number of electrons in various groups.					Bohr's magneton number.
	K_{11} to O_{32}	O_{32}	O_{33}	P_{11}	P_{6}	
77 Ir	68	7	0	2		
Ir^{+++}	68	4	2	0		
Ir^{+++}complex	68	4	6	2	6	Diamagnetic.
Ir^{++++}	68	3	2	0		
Ir^{++++}complex	68	4	6	1	6	
78 Pt	68	8	0	2		
Pt^{++++}	68	0	6	0		Diamagnetic (Rây and Bhar, *private communication*).
Pt^{++++}complex	68	4	6	2	6	Diamagnetic.

It will be found that the trivalent iridium, rhodium and tetravalent platinum complexes possess quite closed configurations like the cobalt complex and hence they will be as stable as the latter and will be likewise diamagnetic. This is in close agreement with facts as far as they are known (Rosenbohm, *Zeit. phys. Chem.*, 1919, **93**, 693). Tetravalent iridium complexes having a lone electron in N_{11} subgroup resemble ferric complexes and like the latter are comparatively unstable and are known only in the case of a few strongly associating units.

Molybdenum complexes having a configuration similar to that of chromium complexes behave like the latter.

Finally some eightfold stable co-ordination complexes of molybdenum and tungsten as well as some fourfold stable complexes of palladium and platinum need be discussed here. The following types of very stable compounds of Mo and W are known.

$$K_4\left[\overset{IV}{Mo}(CN)_8\right];\ K_4\left[\overset{IV}{W}(CN)_8\right];\ K_3\left[\overset{V}{W}(CN)_8\right].$$

Possible electronic configurations for these compounds are represented in Table IV below.

Table IV.

	Number of electrons in various groups.				
Name.	K_{11} to N_{22}	N_{23}	N_{33}	O_{11}	O_3
42 Mo	36	4	..	2	...
Mo^{++++}	36	...	2	...	...
Mo^{++++}complex	36	4	6	2	6
	K_{11} to O_{33}	O_{23}	O_{33}	P_{11}	P_3
74 W	68	4	...	2	...
W^{++++}	68	...	2	...	...
W^{++++}complex	68	4	6	2	6
W^{+++++}	68	...	1	...	...
W^{+++++}complex	68	4	6	1	6

As regards the positive ions of molybdenum and tungsten nothing can be definitely stated about their configurations—in fact there are no free positive ions of Mo and W known in solution as the electropositive character of these elements is very weak. Simple compounds of Mo and W can be more appropriately regarded as nonpolar compounds. It is for this reason that they form no positive complexes—all molybdenum and tungsten complexes being electro-negative or neutral in character. The configurations of the ions of these elements represented in the above table are meant only to indicate the mechanism of formation of the corresponding complexes. Here as usual 12 out of the 16 shared electrons are equally distributed either between the N_{23} and O_3 levels in the case of molybdenum or between O_{23} and P_3 levels in tungsten. The rest four goes to N_{33} in molybdenum or to O_{33} in tungsten. In the case of pentavalent tungsten complex, there is one lone electron in P_{11}. This makes them somewhat less stable. From the nature of the configuration it can be expected that the pentavalent tungsten complexes should exhibit paramagnetism while both the tetravalent Mo and W complexes would be diamagnetic. This has yet to be proved.

We now pass on to the fourfold stable complexes of palladium and platinum, their configurations being shown in Table V.

In these fourfold complexes the 8 shared electrons are distributed equally between N_{22} and O_{22} or between O_{22} and P_{22}. Such compounds should be diamagnetic. This is borne out by facts.

Table V.

Name.	Number of electrons in various groups.						
	K_{11} to N_{22}	N_{21}	N_{23}	O_{11}	O_{21}	O_{22}	
46 Pd	36		10			(McLennan, McLay and Smith, *Proc. Roy Soc.* A 112, 1926)	
Pd^{++}	36	...	6	2		Diamagnetic (Bose, *private communication*).	
Pd^{++} complex	...	4	6	2		4	
	K_{11} to O_{22}	O_{21}	O_{23}	P_{11}	P_{21}	P_{22}	
78 Pt	68	...	10	...	...	...	...
Pt^{++}	68	...	6	2	...	...	
Pt^{++}complex	68	4	6	2	...	4	Diamagnetic

From an examination of the electronic distribution in all the complexes discussed above it will be observed that the electronic orbits of the co-ordinating atoms are likely to be considerably strained or distorted due to the sharing of electrons with the central ion in different levels. That such a distortion of orbits does take place has been assumed by Fajans (*Naturwissenschaften*, 1923, **11**, 165), even in the case of many simple compounds. Meisenheimer (*Zeit. phys. Chem.*, 1921, **97**, 304) regards this distortion of orbits as the cause of colour in chemical compounds. In the case of complex compounds it is observed that the colour of the central ion is profoundly altered by co-ordination and the colour of the complex also varies characteristically with the nature of the associated units. Thus a co-ordinated nitrogen atom in the form of NH_3 or NO_2 group tends to develop a yellow colour in the complex as in hexammine salts and cobaltinitrites ; a sulphur atom in association as SO_2 radical produces brown

to yellowish brown colour and an oxygen atom as in CO_3 or SO_4 radical gives rise to violet to red-violet colour ; halogen atoms as in chloropentammine compounds produce carmine red colour. This colour change according to Meisenheimer (*loc. cit.*) is due to the distortion of the electronic orbits. And this distortion of orbits can be easily accounted for if we assume the scheme depicted above for the configuration of the complexes. As in them every two electrons of each shared pair enter two different levels of the central ion,—a condition most likely to lead to a considerable distortion of the electronic orbits of the co-ordinated groups. This becomes a source of great strain in the complex. It makes them somewhat less stable than the simple non-polar compounds.

Last of all we shall discuss the case of the weak or imperfect complexes. To this class belong almost all complex compounds of nickel. copper, zinc, cadmium, cobaltous cobalt and various other elements. Compounds of this class, *e.g.*, $CuSO_4.5NH_3$, $CuSO_4.4NH_3$, $NiCl_2.4NH_3$, $NiCl_2.6NH_3$ etc., more or less easily lose their complex character even by thermal or other physical disturbances. Hydrates like $CuSO_4.5H_2O$, $FeSO_4.7H_2O$ etc. may be included in this class. Their stepwise dissociation with rise of temperature as determined by Biltz and Huttig (*Zeit. anorg. Chem.*, 1922 **123**, 42) points to a differentiation among the associated units, which shews that all the associated units are not equally strongly held by the central ion. So in their case, it quite stands to reason to assume that the different units share electrons with the central ion at different levels. Thus in the case of $CuSO_4.5NH_3$ for instance all the five ammonia molecules have not the same binding strength. One or two of them may share electrons in one single level, another in another level and a third in a still different level and so on. This is demonstrated by the following electorn distribution in them (Table VI).

The magnetic moment of these complexes according to this scheme should remain practically unchanged. This is actually borne out by facts as indicated by the last column. Almost all determinations of the magnetic moment of these compounds indicate that the values depend entirely on the paramagnetic ion and are not influenced by association (Rosenbohm, *Zeit. phys. Chem.*, 1919, **93**, 693). In some instances as in fourfold nickel complexes the magnetic moment has been found to be somewhat less than that of the free central ion. This may be due to some rearrangement

giving rise to a more stable configuration as suggested by Cabrera and shown below:—

	Number of electrons.				
	K_{11} to M_{32}^{-}	M_{33}	M_{33}	(N_1 to N_3)	
Ni^{++}	18	4	4	...	...
Fourfold Ni^{++}complex	18	4	4	4	4

TABLE VI.

Name.	Number of electrons in different levels.									Bohr's magneton number.
	K_{11} to M_{32}^{-}	M_{32}	M_{33}	N_{11}	N_{21}	N_{22}	N_{32}	O_{11}		
Co^{++}	... 18	3	4	...	...	...	...	...		4
Co^{++}complex (fourfold)	... 18	3	4	2	2	4	...	...		4
Co^{++}complex (sixfold)	... 18	3	4	2	2	4	4	...		4
Ni^{++}	... 18	4	4	...	...	...	...	...		2
Ni^{++}complex (fourfold)	... 18	4	4	2	2	4	...	...		2
Ni^{++}complex (sixfold)	... 18	4	4	2	2	4	4	...		2
Cu^{++}	... 18	4	5	...	...	...	...	...		1
Cu^{++}complex (fourfold)	... 18	4	5	2	2	4	...	...		1
Cu^{++}complex (fivefold)	... 18	4	5	2	2	4	2	...		1
Cu^{++}complex (sixfold)	... 18	4	5	2	2	4	4	...		1

In this case the 8 electorns supplied by the four associating units possibly rearrange themselves in part at least into two groups of 4 each, each binding unit furnishing one electron to each group. A more symmetrical arrangement is thus developed but involving an increased distortion of orbits which is likely to influence the magnetic moment. Such a redistribution leads to the tetrahedral

arrangement of the associated units as in the case of carbon compounds discussed in the beginning. Strongly associating units like dimethylglyoxime. $\beta\beta'\beta''$-triamino-triethylamine are likely to assist this redistribution.

In the light of above discussion this type of imperfect complexes may be termed " Associated Complexes " and consequently the perfect class as " Penetration Complexes " since in the latter case a more or less inner level of electrons takes part in the sharing.

Summary.

In summing up the discussion I would like to emphasise the following points.

Three factors governing the formation of complex compounds should be recognized:

(*a*) Charge on the central ion which is the source of attraction.

(*b*) Tendency of the central ion to assume the next higher inert gas configuration.

(*c*) The nature of the electron distribution in the central ion.

In the case of penetration or strong complexes both the factors (*a*) and (*b*) operate strongly; the third factor (*c*) acts as a controlling factor and determines the nature of the complex formation and the type of co-ordination.

The factor (*a*) also involves the influence of the volume of the ion—the smaller is the volume, the stronger is the attraction.

In discussing the electron-distribution in the central ion from the chemical standpoint the following simple assumptions were made and found very useful.

Every two electrons tend to couple closely. A lone electron in a comparatively outer subgroup is rather unstable. The stability of any subgroup increases with the number of electrons in it.

From these assumptions a scheme for electron-distribution in strong and weak complexes has been suggested. Tendency to assume the external electronic configuration of the next higher inert gas by the central ion is upheld as the main guiding factor in the formation of penetration or perfect complexes.

My best thanks are due to Prof. Dr. D. M. Bose for much useful informations I have received from him.

Note.—Since this paper was completed in April, 1927 some other papers have appeared on the subject. Prof. Ladenburg in a lecture before the German Chemical Society (*Zeit. phys. Chem.*, 1927, **126**, 133) expressed the view that two types of co-ordinated compounds should be recognized,—stable and less stable. The diamagnetism of a complex compound according to him arises from the complete filling up of the intermediate sub-groups of the central atom with electrons. This is in agreement with the view elaborated in this paper.

Two other papers on " Co-ordination bond and atomic structure " have also been published lately by Lessheim, Meyer and Samuel (*Zeit. Physik*, 1927, **43**, 199 ; *Zeit. anorg. Chem.*, 1927, **165**, 253). According to these authors co-ordinative binding is effected by the electrons of the outermost completely filled up sub-group ("Teilunter" group). They assume one electron bond which is rather unique and take no cognisance of Sidgwick's conception. What is specially objectionable in their view is that they make an atom which has already completed its octet or assumed an inert gas configuration (as for instance N atom in NH_3 mol) to share a further electron supplied by the central ion thus making the total number of electrons round the nitrogen atom eleven which is most unlikely.

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The Sodium and Potassium Phenolates.

By

Andrew Norman Meldrum and (the late) Mankanji Motiram Patel.

The sodium and potassium phenolates have been prepared in a variety of ways. Potassium phenolate, for instance, was prepared (1) by heating phenol with solid potassium hydroxide (Hartmann, *J. pr. Chem.*, 1877, (*ii*), **16**, 38), (2) from phenol and potassium whilst a current of hydrogen was passed (*loc. cit.*, p. 36); (3) by mixing solutions in alcohol of phenol and potassium ethoxide and evaporating (de Forcrand, *Ann. Chim. Phys.*, 1893 (*vi*), **30**, 61); (4) by boiling phenol with a solution of potassium carbonate (Baumann, *Ber.*, 1877, **10**, 686). These methods have various disadvantages: the first gives crude material: the second and third are expensive: the third is also troublesome because the last traces of alcohol are not easily removed from the phenolate; moreover, these methods are unnecessary except in special cases.

A simple method of preparing potassium phenolate, as the authors found, is to dissolve phenol in an ordinary aqueous solution of potassium hydroxide and then to add a concentrated solution of the same alkali: crystalline potassium phenolate is precipitated and can be isolated in a relatively pure state.

This method is comparable with the precipitation of a metallic chloride from solution by means of hydrochloric acid. It is a general method; the authors used it for the preparation of a number of sodium and potassium phenolates. These phenolates have definite melting points: when the melting point is low the phenolate separates as a liquid, *e.g.*, sodium *o*-cresolate. In no case did the phenolate contain water of crystallisation.

It is to be observed that the solubility of a phenolate is an important property that may be useful in the isolation of a phenol. This is illustrated in the next paper, where two phenolic substances, namely 3-nitro- and 5-nitro-salicylic acids, are separated and purified by means of their potassium compounds.

No difficulty was found in obtaining derivatives from these substances: potassium phenolate was converted into phenyl benzoate and into diphenyl ether: sodium *p*- and *m*-cresolates were converted into the respective benzoates.

Experimental.

The composition of the solutions that were used in the experiments is shown in the following table:—

	Alkali in water (100 c.c.)	
	NaOH	KOH
Ordinary solution	20 g.	28 g.
Strong ,,	100 g.	100 g.
Very strong ,,	...	200 g.

Usually it was sufficient to dissolve the phenol in the minimum amount of ordinary solution and then to add the strong solution. In special cases it was necessary, the phenolate being comparatively insoluble, to dilute the ordinary solution before use: the phenolate being comparatively soluble, to precipitate by means of the very strong solution: the phenolate having a low melting point, to cool by means of a freezing mixture; these cases are mentioned as they arise.

The crystalline precipitate was collected, using a Buchner funnel, with the aid of the pump, and was drained for some time so that by absorption of moisture from the air the crystals were freed from the adhering alkaline solution. At the same time foreign material, such as suspended matter from the alkaline solutions, was found to collect in a layer below. The crystals were next pressed on a porous tile and the tile was kept in a desiccator.

For analysis the phenolate, having been pressed again on a clean, dry, porous tile, was converted into sodium or potassium sulphate.

Only the usual precautions were taken in observing the melting points which may therefore be slightly low.

Sodium phenolate was obtained as needle-shaped crystals, m.p. 59-60°. (Found: Na, 19·6. C_6H_5ONa requires 19·8 per cent.).

Potassium phenolate was obtained as small needles that changed into plates, m.p. 103-104°. (Found K, 29·4. C_6H_5OK requires 29·6 per cent.).

Sodium o-*cresolate* was obtained as a liquid that solidified below 0°.

Potassium o-*cresolate* was obtained with difficulty as needle-shaped crystals. It is very hygroscopic.

Sodium p-*cresolate* was obtained as long needles that changed into glistening plates, m.p. 123-125°. (Found: Na, 17·8. C_7H_7ONa requires 17·7 per cent.).

Potassium p-*cresolate* was obtained as glistening plates, m.p. 92°. (Found: K, 26·2. C_7H_7OK requires 26·7 per cent.).

Sodium m-*cresolate* was obtained, using diluted sodium hydroxide for dissolving, as glistening plates, m.p. 92-94°. (Found: Na, 17·5. C_7H_7ONa requires 17·7 per cent.).

Potassium m-*cresolate* was obtained, using very strong potassium hydroxide for precipitating, as small prisms, m.p. about 36°. It is very hygroscopic. (Found: K, 26·9. C_7H_7OK requires 26·7 per cent.).

Sodium m-*xylenolate* formed slowly as minute crystals, m.p. 41-43°. (Found: Na, 15·7. C_8H_9ONa requires 16·0 per cent.).

Potassium m-*xylenolate* was obtained only as a liquid.

Sodium p-*xylenolate* was obtained as glistening plates, m.p. 83°. (Found: Na, 16·1. C_8H_9ONa requires 16·0 per cent.).

Potassium p-*xylenolate* was obtained, using very strong potassium hydroxide for precipitating and using a freezing-mixture, as granular crystals, m.p. 35°. (Found: K, 24·4. C_8H_9OK requires 24·4 per cent.).

Sodium guaiacolate was obtained, using diluted sodium hydroxide solution, as small crystals, m.p. 120°. (Found: Na, 15·6. $C_7H_7O_2Na$ requires 15·7 per cent.).

Potassium guaiacolate was obtained, using diluted potassium hydroxide solution, as small crystals, m. p. 168°. (Found: K, 24·0. $C_7H_7O_2K$ requires 24·1 per cent.).

Sodium eugenolate was obtained, using diluted sodium hydroxide solution for dissolving, as shining plates, m.p. 115°. (Found: Na, 12·6. $C_{10}H_{11}O_2Na$ requires 12·4 per cent.).

Potassium eugenolate was obtained, using diluted potassium hydroxide solution for dissolving, as prismatic crystals, m.p. 128°. (Found: K, 19·3. $C_{10}H_{11}O_2K$ requires 19·3 per cent.).

Sodium α-naphtholate was obtained, on cooling, as small crystals, m.p. 44-45°. (Found: Na, 14·4. $C_{10}H_7ONa$ requires 13·8 per cent.).

Potassium α-naphtholate was obtained only as a liquid.

Sodium β-naphtholate was obtained, using diluted sodium hydroxide for dissolving, as small plates, m.p. 120°. (Found: Na, 13·9. $C_{10}H_7ONa$ requires 13·8 per cent.).

Potassium β-naphtholate was obtained as small plates, m.p. 38-40°. (Found: K, 21·5. $C_{10}H_7OK$ requires 21·5 per cent.).

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Derivatives of Salicylic Acid. Part I. 3-Nitro- and 5-Nitro-salicylic Acids.

By Andrew Norman Meldrum and Narhar Waman Hirve.

In continuation of work done by Meldrum and Shah on sulphosalicylic acid (*J. Chem. Soc.*, 1923, **123**, 1986) it was intended to prepare the nitrosulphosalicylic acids. For this purpose it was necessary to obtain the 3-nitro- and 5-nitro-salicylic acids.

Work on the preparation of these acids, from salicylic acids, has been done by Griess (*Ber.*, 1878, **11**, 1730), Hübner (*Annalen*, 1879, **198**, 258), Deninger (*J. pr. Chem.*, 1890, (*ii*), **42**, 550) and by Meldola, Foster, and Brightman (*J. Chem. Soc.*, 1917, **111**, 536). The last named authors heated salicylic acid with dilute nitric acid on the water-bath for an hour: they isolated only 5-nitrosalicylic acid. Deninger used nitrous acid; he stated that at a high temperature 3-nitrosalicylic acid, and at a low temperature 5-nitrosalicylic acid is produced.

Following closely the methods of Meldola, Foster and Brightman and of Deninger, we obtained always a mixture of the 3- and 5-nitro acid. We found also that the separation of these acids with the help of their barium salts, recommended by Hübner, is slow and uncertain. We have, therefore, devised a simple method of nitration, and also a method of separating the two isomers that depends on the properties of the mono- and the di- potassium salts. The appearance and the solubilities of these salts are given in the following table:—

Salt.	*3-Nitro acid.*	*5-Nitro acid.*
$HO{\cdot}C_6H_3{\cdot}NO_2{\cdot}COOK$.	Pale yellow wisps of needles; solubility 0·94 (31°).	Shining golden yellow needles; easily soluble in water: Solubility 6·60 (31°).
$KO{\cdot}C_6H_3{\cdot}NO_2{\cdot}COOK$.	Crimson-red needles, soluble in potassium hydroxide solution.	Yellow needles, difficultly soluble in potassium hydroxide solution.

The 3-nitro acid can be separated as monopotassium salt, and the 5-nitro acid as the dipotassium salt: each salt can then

be purified. Moreover, it is possible to acertain, approximately, how much of each acid is produced during nitration.

The older methods of separation by crystallisation of the acids or of their barium salts yield the 5-nitro acid in the pure state, whilst the 3-nitro acid is not obtained pure. Generally it can be said that the recorded work on 3-nitrosalicylic acid and its derivatives is unreliable; this can be seen from the following tables, the first of which gives the melting points of the acids.

	Melting points.	
	Previous workers.	Meldrum and Hirve.
3-Nitro-salicylic acid (hydrated).	125°	128-129°
,, (anhydrous).	145°	148-149°
5-Nitro-salicylic acid.	228°	228°

The Methyl Esters.

Knowledge of the methyl esters of 3-nitro- and 5-nitro-salicylic acids was uncertain and confused: in Beilstein's *Handbuch der Organischen Chemie*, 1896, **2**, 1509), they are described as ethyl esters. Smith and Knerr (*Am. Chem. J.*, 1886, **8**, 49), by passing nitrogen trioxide into a solution in ether of methyl salicylate, obtained two substances neither of which is correctly named by these authors. Keller (*Arch. Pharm.*, 1908, **246**, 1) by various methods obtaind from 3-nitrosalicylic acid (m. p. 144°) three methyl derivatives for one of which he could not account. We prepared each ester from methyl alcohol and the respective acid. The following table gives the observed melting points.

	Smith and Knerr.	Keller.	Meldrum and Hirve.
Methyl 3-nitro-salicylate	118°	98°	132°
Methyl 5-nitrosalicylate	96°	...	119°

By following Smith and Knerr's method we obtained a mixture from which we separated three substances, m. p. 132°, 118°, and 96° respectively. Of these the first is methyl 3-nitrosalicylate and the second (named in error by Smith and Knerr) is methyl 5-nitrosalicylate. The third, m. p. 96°, we found to be a eutectic mixture: when hydrolysed by potassium hydroxide it was possible to separate

the characteristic potassium salts of 3-nitro- and 5-nitrosalicylic acids. Keller's substance, m. p. 93°, can be accounted for as being nearly the same as the eutectic mixture, and as having been obtained from a specimen of the 3-nitro acid that was contaminated with the 5-nitro acid.

*The Ethyl Esters.**

Ethyl 3-nitrosalicylate was prepared by Hübner (*Annalen*, 1879, **195**, 34) from the silver salt and ethyl iodide and by Zacharios (*J. pr. Chem.*, 1871, (ii) **43**, 434) from alcohol and the acid in presence of sulphuric acid.

Ethyl 5-nitrosalicylate was prepared by Hübner (*loc. cit.*) from the silver salt and ethyl iodide. Thieme (*J. pr. Chem.*, 1891, (ii), **43**, 469) and Herre (*Ber.*, 1895, **28**, 498) prepared it from alcohol and the acid in presence of sulphuric acid. We prepared these substances from alcohol and the respective acids. The following table gives the observed melting points:—

	Hubner.	Zacharios.	Herre.	Thieme.	Meldrum and Hirve.
Ethyl 3-nitrosalicylate	...	44·5°	...	...	48·5°
Ethyl 5-nitrosalicylate	93°	...	96°	96°	102°

The Amides.

Hübner (*Annalen*, 1879, **198**, 35) prepared the amides by heating together the respective ethyl esters and alcoholic ammonia. We prepared them by shaking a mixture of the respective ethyl esters, alcohol and ammonia solution. From the resulting mixture of the amide and the ammonium salt we precipitated the amide by means of potassium hydroxide solution in the case of the 3-nitro-acid: the potassium salt of the acid is precipitated first and then that of the amide; in the case of the 5-nitro acid the potassium salt of the amide is first precipitated.

* Hirsch (*Ber.*, 1900, **33**, 3239) reported a method by which he obtained (*a*) 3-nitrosalicylic acid, m. p, 144°, and its ethyl ester, m. p. 118°; (*b*) 5-nitrosalicylic acid, m. p. 230°, and its ethyl ester, m. p. 93°. There is no proof that the substances, m. p. 118° and m. p. 93°, were ethyl esters or pure substances. No analyses are given.

	Hubner.	Meldrum and Hirve.
3-Nitrosalicylamide ...	145-146°	155°
5-Nitrosalicylamide ...	225°	225°

Experimental.

Numerous experiments have led to the following details for the preparation and the separation of 3-nitro- and 5-nitro-salicylic acids.

Nitration.—Salicylic acid (100 g.) was mixed with nitric acid (*d* 1·2 ; 200 c. c.). The mixture was well shaken from time to time and kept cool. After twenty-four hours it was shaken automatically for two hours. The solid product was then collected by filtration and washed with water.

Separation.—The solid was dissolved in a hot concentrated solution of potassium carbonate so that the solution, being neutral to litmus, contained the mono-potassium salts. The less soluble salt (of the 3-nitro-acid) separated as pale yellow needles. A further yield was obtained by concentrating the filtrate. The mother-liquor was rendered alkaline by strong potassium hydroxide. The composition of the salts at this stage is $C_6H_3.NO_2.COOK.OK$: this salt of the 5-nitro acid separated as yellow needles. The mother-liquor was neutralised by acetic acid and a further yield of the potassium salt of the 3-nitro acid was obtained. The final mother-liquor contained the potassium salts of the nitro acids, unchanged salicylic acid and *o*-nitrophenol in small amounts.

The salts were recrystallised from water. The respective acids were liberated on addition of dilute sulphuric acid to the aqueous solution of pure salts and were finally recrystallised from water.

We also studied the methods for nitration laid down by previous workers using our own method of separating the nitro acids. In each experiment 100 g. of salicylic acid were used. The results are shown in the following table:—

Nitration of Salicylic Acid.

Authors.	Nitrating agent.	Temperature.	Yield 3-Nitro acid.	Yield 5-Nitro acid.	*o*-Nitrophenol.
Meldrm and Hirve.	HNO_3 (*d* 1·2) 200 c. c.	Room temperature.	33·5 g.	55 g.	Little.
Meldola, Foster and Brightman.	One part HNO_3 and four parts water.	100° for one hour.	22·5 g.	50 g.	Much.
Deninger (for 3-nitro-).	$NaNO_3$ and H_2SO_4 (*d* 1·52)	Free rise of temperature.	15 g.	22·5 g.	Much.
Deninger (for 5-nitro).	$NaNO_3$ and H_2SO_4 (*d* 1·52)	Below 15°, finally warming to 50°.	15 g.	20 g.	Little.

3-Nitrosalicylic acid forms long yellowish-white needles, $C_7H_5O_5N$, H_2O, m. p. 128-129°. The anhydrous acid is yellow, m. p. 148-149°. (Found: H_2O, 8·95. $C_7H_5O_5N$, H_2O requires H_2O, 8·96 per cent.).

Potassium Salt.—(Found: K, 17·65. $C_7H_4O_5NK$ requires K, 17·65 per cent.).

The phenolic potassium salt was prepared by adding excess of strong potassium hydroxide solution to the acid. Red coloured microscopic needles separated from the solution, which were collected and washed with a little alcohol. On standing the substance absorbs moisture turning yellow, and changes again to red on heating. (Found: K, 30·63. $C_7H_3O_5NK_2$ requires K, 30·11 per cent.).

Barium Salts.—In accordance with previous work our analysis showed that the composition of the neutral barium salt is $(C_7H_4O_5N)_2Ba$ (the solubility at 31° is 0·15): that of the phenolic barium salt is $C_7H_3O_5NBa$, $1\frac{1}{2}$ H_2O.

5-Nitrosalicylic acid crystallises in long white needles, m. p. 228°. It is difficultly soluble in water and easily soluble in acetic acid, alcohol and ether.

Potassium 5-nitrosalicylate was prepared by adding the acid to strong potassium carbonate solution till it was neutral to litmus. The properties are given above. (Found: K, 17·32. $C_7H_4O_5NK$ required K, 17·65 per cent.).

The phenolic potassium salt was obtained by adding strong potassium hydroxide solution to the above neutral salt or to the acid itself. It crystallises as yellow needles. (Found: H_2O, 11·85; K, 26·52. $C_7H_3O_5NK_2$, $2H_2O$ requires H_2O, 12·20; K, 26·44 per cent.).

Barium Salts.—In accordance with previous work, our analyses showed that the composition of the neutral barium salt is $(C_7H_4O_5N)_2Ba$, $4H_2O$ (the solubility at 31° is 1·33): that of the phenolic barium salt is $C_7H_3O_5NBa,H_2O$.

Methyl 3-Nitrosalicylate.—Pure dehydrated 3-nitrosalicylic acid (15 g.) was dissolved in methyl alcohol (60 c.c.) and dry hydrochloric acid gas (6 g.) was passed into it. The mixture was refluxed on the water-bath for four hours. On cooling crystals separated which were collected; a further yield was obtained from the mother-liquor on evaporation.

It is slightly soluble in methyl and ethyl alcohols, cold ether, cold chloroform, and benzene.

It crystallised from ethyl alcohol in beautiful octahedra of a pale yellow colour, m.p. 132°; yield 15 g. (Found: N, 7·11. $C_8H_7O_5N$ requires N, 7·10 per cent.)

Methyl 5-nitrosalicylate was prepared in a similar way. The excess of alcohol was removed by distillation. It recrystallised from ethyl alcohol in long white needles, m.p. 119°.

It is easily soluble in ether, cold chloroform and benzene and less easily soluble in ethyl and methyl alcohols. (Found: N, 7·39. $C_8H_7O_5N$ requires N, 7·10 per cent.).

With a view to account for the substance, m.p. 96°, obtained by Smith and Knerr (*loc. cit.*), we prepared it by their method obtaining at the same time substances identical with our methyl esters. The substance was hydrolysed by potassium hydroxide, and from the hydrolysed mixture 3-nitro- and 5-nitro-salicylic acids were obtained separately by the method adopted for the separation in this paper. The substance, m.p. 96° (1·2 g.), gave the 3-nitro acid (0·25 g.) and the 5-nitro acid (0·7 g.).

Ethyl 3-Nitrosalicylate.—Pure anhydrous 3-nitrosalicylic acid (18 g.) was dissolved in absolute alcohol (72 c.c.) and dry hydrochloric acid gas (8 g.) was passed into it, and the mixture was refluxed on the water-bath for 6 hours. On cooling an oily layer separated, which crystallised slowly; the mother-liquor on evaporation gave a further yield: total 16·5 g.

Ethyl 3-nitrosalicylate is readily soluble in methyl and ethyl alcohols, acetic acid, chloroform and slightly soluble in cold petroleum ether and benzene. From petroleum ether it separates in well defined cubes, m.p. 48·5°. (Found: N, 6·67. $C_9H_9O_5N$ requires N, 6·63 per cent.).

Ethyl 5-Nitrosalicylate.—Pure 5-nitrosalicylic acid (30 g.) was dissolved in absolute alcohol (120 c.c.) and dry hydrochloric acid gas (11 g.) was passed into it, and the mixture was refluxed on the water-bath for about 5 hours: on cooling, the ester separated in long slender needles. The mother-liquor, on evaporation, gave a further yield: total 27 g.

Ethyl 5-nitrosalicylate is easily soluble in hot acetic acid and alcohol and difficultly soluble in cold acetic acid, alcohol, ether and benzene: easily soluble in chloroform. It can be best crystallised from acetic acid or alcohol, from which it is obtained as long slender

needles, m.p. 102°. (Found: N, 6·66. $C_9H_8O_6N$ requires N, 6·63 per cent.).

3-*Nitrosalicylamide*.—Ethyl 3-nitrosalicylate (10 g.) was dissolved in absolute alcohol (100 c.c.) in a glass stoppered bottle, and cooled. Strong ammonia solution (200 c.c.) was added to it, when the ester was precipitated. This mixture was automatically shaken until a clear solution was obtained. After driving away the excess of ammonia by heating on the water-bath, the solution was acidified, and the resulting precipitate was neutralised by potassium hydroxide solution, when potassium 3-nitrosalicylate was precipitated. On adding strong potassium hydroxide solution to the mother-liquor, the potassium salt of the amide was precipitated. It was collected, washed, dissolved in water again, and the amide liberated by acidifying. The pure substance was obtained on recrystallising it from water in pale yellow needles, m p. 155°.

3-*Nitrosalicylamide* is very soluble in acetic acid and nitrobenzene, easily soluble in ethyl alcohol and hot water, difficultly soluble in chloroform and benzene and insoluble in petroleum ether. (Found: N, 15·52. $C_7H_6O_4N_2$ requires N, 15·39 per cent.).

The *potassium salt* was recrystallised from water: small orange coloured needles. (Found: K, 16·43. $C_7H_5O_4N_2K$, H_2O requires K, 16·39 per cent.).

5-*Nitrosalicylamide*.—Ethyl 5-nitrosalicylate (20 g.) was dissolved in absolute alcohol (100 c.c.) and then strong ammonia solution (30 c.c.) was added, when the ester was precipitated. The amide was prepared and purified as in the preceding case.

It was crystallised from methyl alcohol: needles and rectangular plates, m.p. 225°.

5-*Nitrosalicylamide* is extremely soluble in nitrobenzene, easily soluble in acetic acid, moderately soluble in methyl and ethyl alcohol, difficultly soluble in petroleum, ether and benzene and insoluble in chloroform. (Found: N, 15·50. $C_7H_6O_4N$ requires N, 15·39 per cent.).

The potassium salt ($C_6H_3.NO_2.OK.CONH_2,H_2O$) crystallised from water in cluster of yellow silky needles: (Found: H_2O, 7·52; K, 16·43. $C_7H_5O_4NK$, H_2O requires H_2O, 7·56; K, 16·39 per cent.).

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Aluminium Powder as a Synthetic Reagent.

By Amaresh Chandra Ray and Sikhibhushan Dutt.

Since the middle of the 19th century, various metals have been used in the different processes of organic synthesis, but the metal aluminium has not received as wide applications although its salts, particularly the anhydrous chloride and to a certain extent the amalgam have been used in the well-known Friedel-Craft's synthesis. Perhaps the first important attempts to treat metallic aluminium with organic substances were those of Gladstone and Tribe (*J. Chem. Soc.*, 1876, **29**, 158; 1881, **39**, 1) who prepared aluminium alcoholates by the action of alcohols on the metal. Their work was subsequently extended and criticised by Saligman and Williams (*J. Chem. Soc.*, 1918, **113**, 159), who prepared the aluminium salts of fatty acids, alcohols and phenols by the action of purified aluminium powder on the corresponding dry substances at their respective boiling points. They also showed that the reactions are entirely inhibited by traces of moisture even when once started, and this phenomenon has been explained by them as due to the formation of a superficial layer of oxide.

In 1895, an attempt was made by Radziewanoski (*Ber.*, 1895, **28**, 1139) to use aluminium powder mixed with mercuric chloride as a condensing agent in the ordinary Friedel-Craft's reaction, but it was a failure. Later on he found (*Ber.*, 1904, **37**, 1560) that aluminium powder in benzene or xylene solution formed compounds with mercuric chloride of the type C_6H_6. $AlCl_3$. HgCl, which gave successful results in several condensations of the type of Friedel-Craft's reaction. Subsequently this work has been extended by Ray (*J. Chem. Soc.*, 1920, **117**, 1335).

The above represents practically the whole of the literature on the reactions of aluminium powder, from which it can be easily seen that aluminium powder has hardly been used in the condensations apparently due to its inactivity, and in those few scattered examples in which use has been made of the metal, it has been either amalgamated with mercury or mixed with such substances as mercuric chloride or hydrogen chloride. Therefore the present investigation was undertaken with a view to make an

exhaustive study of the metal in many of the typical reactions of organic chemistry.

It was found that ordinary aluminium powder is very inactive. Washing with caustic soda and acid, refluxing for several hours with ether, alcohol or benzene did not make much improvement. The problem was becoming almost hopeless, when incidentally it was found that aluminium powder becomes highly reactive when heated in a current of pure dry hydrogen at about 500° for a short time. This peculiar phenomenon was at first thought to be due to the formation of a metallic hydride, but since on quantitative analysis the metal thus activated is found to contain no hydrogen, it is supposed that the activation is due to the reduction of the film of suboxide with which the surface of ordinary metallic aluminium is always covered. The existence of such a suboxide has not been recorded in inorganic literature, the only oxide on record being Al_2O_3. But as it is well known that the latter oxide cannot be reduced by hydrogen, so the presence of a sub-oxide is fairly tentative as in the case of lead. Aluminium thus activated has been found to react vigorously with oxygenated and halogenated compounds in accordance with the well known and typical reactions of Ullmann, Friedel and Craft, Wurtz, Reformatski and others. Aluminium under such conditions also acts as a strong pyrogenetic and neutral reducing agent.

Thus it is seen that aluminium powder when properly activated by heating in a current of pure dry hydrogen behaves almost exactly like copper, silver, mercury or zinc in most of the typical organic reactions. The only notable exception with regard to the behaviour of aluminium is that it does not form an organo-metallic derivative like magnesium in Grignard's reaction under the same circumstances. Otherwise aluminium powder is a very reactive material with which a large number of organic syntheses can be achieved.

Experimental.

Dry Distillation with Aluminium Powder.

In these series of experiments, fine commercial aluminium powder was refluxed with absolute alcohol for several hours and then very thoroughly washed with ether. The metallic powder thus purified was then carefully dried at 110°, and stored in stoppered bottles until required for use. For the purpose of dry distillation

a hard glass tube about 30 inches in length was bent at about 8 inches from one end, so as to form a delivery tube to which a distilling flask was attached as a receiver. This latter was carefully cooled by cold water, ice or freezing mixtures according to the nature of the compound undergoing distillation. The longer portion of the tube was packed to about three quarters of its length with broken pumice which had been previously coated with the prepared aluminium dust. The rest of the tube at the other end was filled with the substance intimately mixed with three times its weight of the same aluminium powder. A slow stream of pure and carefully dried hydrogen or carbon dioxide was then passed through the tube while the latter was heated in a combustion furnace, taking care to heat the substance last of all. In this way many substances were distilled and all the various products isolated and identified. The results are summarised in tabular form.

Dry distillation with aluminium powder in a current of dry hydrogen or carbon dioxide.

Substance.	Temperature of distillation.	Main product of reaction and percentage of yield (in brackets).	Bye-products.
Phenol	470°	Benzene (21)	Diphenyl.
Catechol	500°—540°	Benzene (15)	Phenol, diphenyl.
Resorcinol	,,	,, (19)	,, ,,
Quinol	,,	,, (12)	,, ,,
Pyrogallol	,,	,, (12)	Catechol, phenol, diphenyl.
Phloroglucinol	,,	,, (18)	Resorcinol, phenol, diphenyl.
p-Nitrophenol	,,	Aniline (23)	Benzene, ammonia, *p*-aminophenol.
m-Nitrophenol	,,	,, (20)	Benzene, ammonia, *m*-aminophenol.
p-Nitrosophenol	,,	,, (21)	Benzene, ammonia, *p*-aminophenol.
m-Nitraniline	,,	,, (15)	Benzene, ammonia, *m*-phenylene diamine.

Substance.	Temperature of distillation.	Main product of reaction and percentage of yield (in brackets).	Bye-products.
p-Nitrotoluene	500°—540°	Toluene (26)	Ammonia, *p*-toluidine.
p-Nitrobenzoic acid	,,	Aniline (13)	Benzene, ammonia, carbon dioxide.
Salicylic acid	,,	Benzene (15)	Phenol, diphenyl, carbon dioxide.
Benzoic acid	,,	,, (15)	Diphenyl, carbon dioxide.
Benzaldehyde	,,	Toluene (39)	*Nil*
Phthalic anhydride	Dull red heat	Phthalide (83)	*Nil*
Quinone	,,	Benzene (13)	Phenol, diphenyl.
Succinimide	,,	Pyrrol (17)	*Nil*
Benzophenone	,,	Diphenylmethane (48)	*Nil*
β-Naphthol	,,	Naphthalene (35)	*Nil*
β-Naphthaquinone	,,	,, (21)	β-Naphthol
Anthraquinone	,,	Anthracene (30)	*Nil*
Phenanthraquinone	,,	Phenanthrene (35)	*Nil*
Alizarine	,,	Anthracene (37)	*Nil*
Isatin	,,	Indol (20)	Aniline
Indigo	,,	,, (12)	,,

Ullmann's Reaction with Aluminium Powder.

(*a*) *Diphenyl from Iodobenzene.*

In this and all other subsequent exeriments described in this paper the aluminium powder immediately before use was heated in a stream of pure, dry hydrogen for about half an hour.

Iodobenzene (10 g.) and aluminium powder (5 g.) were heated under reflux at 250° for about three hours. A vigorous reaction took place and some iodine was deposited in the neck of the flask. The viscous reaction product was extracted with ether, filtered from the unchanged aluminium powder, decolorised with sodium thiosulphate, and allowed to evaporate, when colourless crystals, m.p. 70° were obtained. These were identified to be those of diphenyl (yield 0·43 g.).

(*b*) *Dibenzyl from Benzyl Chloride.*

A mixture of benzyl chloride (10 g.) and aluminium powder (5 g.) was heated under reflux at 200° for about an hour. A vigorous reaction took place and the mass became yellow. On extraction with ether, filtration and slow evaporation a yellow crystalline solid was obtained which melted at 51°, and was identified to be dibenzyl (yield 4·2 g.).

(*c*) *Adipic Acid from β-Iodopropionic Acid.*

β-Iodopropionic acid (6 g.) was intimately mixed with aluminium powder (2·2 g.) and the mixture first heated at 110°-120° for one hour and then at 180°-200° for three hours. The product was cooled and extracted with boiling water. On cooling the extract, large shining colourless crystals separated out. These were filtered off and recrystallised from boiling water, when the substance melted at 148°, and was identified to be adipic acid (yield 1·4 gm.).

(*d*) *Diphenylamine from Aniline and Chlorobenzene.*—Chlorobenzene (10 g.), aniline (9 g.) and aluminium dust (5 g.) were heated at 180°-200° for about three hours. The cold reaction product was then extracted with ether, the ethereal extract filtered from unchanged aluminium powder and allowed to evaporate when a solid crystalline substance was obtained. This on recrystallisation from alcohol melted at 52°, and was identified to be diphenylamine (yield 3·5 g.).

(*e*) *Diphenylether from Phenol and Bromobenzene.*—A mixture of phenol (9 g.), bromobenzene (17 g.), aluminium powder (6 g.) and anhydrous potassium carbonate (0·5 g.) was heated at 180°-200° for about four hours. The reaction product was then distilled in steam, when an oily liquid with a fine flowery smell came over in the distillate. It was extracted with ether, the ethereal extract thoroughly washed with dilute sodium hydroxide and water, dehydrated with calcium chloride and the ether evaporated when a pale yellow liquid was obtained boiling at 252° which was identified to be diphenyl ether (yield 15 gm.).

(*f*) *Hexachloroethane from Carbon Tetrachloride.*—Carbon tetrachloride (15 g.) was heated on the water-bath under reflux with aluminium powder (7 g.) for about half an hour. A vigorous reaction took place and dense white fumes evolved which condensed in the neck of the flask to a colourless crystalline solid. The reaction pro-

duct was isolated by extraction with ether and purified by recrystallisation from benzene when it was obtained in large colourless crystals with a camphor-like smell and melting at 185°. It was identified to be hexachloroethane (yield 9·3 gm.).

FRIEDEL-CRAFT'S REACTION WITH ALUMINIUM POWDER.

(*a*) *Acetophenone from Acetylchloride and Benzene.*—A mixture of carefully dried acetylchloride (10 g.) and benzene (15 g.) was treated with aluminium powder (6 g.) and the whole heated on the water-bath under reflux for about three hours. Torrents of hydrogen chloride were evolved and the mixture set to a dark viscous mass. The product was then carefully treated with ice cold dilute hydrochloric acid when the dark aluminium compound dissolved and a pale yellow oil having the characteristic odour of acetophenone separated out. It was extracted with benzene, dried with calcium chloride and fractionated when a colourless oil boiling at 202° was obtained. This was identified to be acetophenone (yield 9·5 gm.).

(*b*) *Diphenyl Methane from Benzyl Chloride and Benzene.*—A mixture of benzyl chloride and benzene was treated with aluminium powder as in the above instance and the product similarly isolated. It was a colourless oil boiling at 174°-176° and with a pronounced orange-like smell. It was identified to be diphenylmethane (yield about 38 %).

(*c*) *Triphenylmethane from Chloroform and Benzene.*—A mixture of pure dry chloroform (30 c.c.) and benzene (100 c.c.) was treated with aluminium powder (5 g.) and the whole heated on the water-bath for about one hour. A vigorous reaction took place and a copious stream of hydrogen chloride was evolved. After the reaction was over the dark brown aluminium compound was decomposed with ice cold dilute hydrochloric acid and the upper benzene layer separated. This was dried and then distilled, at first on the water-bath at ordinary pressure to remove the excess of benzene, and then over a free flame under reduced pressure (8 mm.). Three fractions were obtained, namely :

(1) A pale yellew oil—3·7 gms. (identified as diphenyl methane).

(2) A colourless crystalline solid—8·6 gms. (identified to be triphenylmethane).

(3) A dark coloured residue—2·7 gms. (which could not be identified).

(*d*) *Triphenyl Methane from Carbon Tetrachloride and Benzene.*—A mixture of carbon tetrachloride (30 g.), benzene (100 g.) and aluminium powder (7 g.) was gently heated on the water-bath under reflux, when a vigorous reaction took place and torrents of hydrochloric acid gas were evolved. In about ten minutes the reaction was over and the whole mass became dark brown in colour. The product was cooled, decomposed with ice cold dilute hydrochloric acid, and from the benzene layer thus separated, diphenylmethane (yield 3·7 g.) and triphenyl methane (yield 11·2 g.) were isolated and identified.

(*e*) *Benzophenone from Benzoyl Chloride and Benzene.*—A mixture of benzoylchloride (15 g.) and benzene (30 g.) was treated with aluminium powder (5 g.) and the mixture heated on the sand-bath under reflux, till the evolution of hydrogen chloride had ceased (about 4 hours). The mixture was then treated with ice cold dilute hydrochloric acid and the benzene layer separated as usual. This was washed with dilute sodium hydroxide and water, dried and fractionally distilled at ordinary pressure, when an almost colourless oil boiling at 300°-310° was obtained. This solidified in the receiver and on recrystallisation from dilute alcohol melted at 46°, and was identified to be benzophenone (yield 3·2 gm.).

Reformatski's Reaction with Aluminium Powder.—A mixture of acetophenone (12 g.), bromacetic ester (17 g.), aluminium powder (5 g.) and dry benzene (100 c.c.) was gently warmed on the water-bath until a vigorous reaction took place. The latter was allowed to subside and then the mixture gently boiled on the sand-bath for about two hours. After cooling, ice cold dilute hydrochloric acid was added to decompose the dark coloured aluminium compound, the benzene layer separated, washed with dilute sodium hydroxide and water, dried and then fractionally distilled under highly reduced pressure. A colourless liquid boiling at 120°/4 mm. was obtained which was identified to be β-phenylmethyl-hydroxy-propionic ester. (yield 6·2 g.).

Neutral Reduction with Aluminium Powder.

(*a*) *Phenyl-hydroxylamine and Aniline from Nitrobenzene.*—A mixture of nitro-benzene (20 g.), ammonium chloride (6 g.), distilled water (250 c.c.) and aluminium powder (16 g.) was vigorously agitated while being cooled in a freezing mixture. A vigorous reaction took place and in about an hour the smell of nitrobenzene had

completely disappeared. The solution was filtered at the pump, the residue washed with about 100 c.c. of ice cold water, and the combined filtrate and washings saturated with salt and left standing in the freezing mixture, when the liquid became almost semi-solid with deposit of fine colourless crystals. These were identified to be those of phenyl-hydroxylamine (yield almost quantitative).

The reaction was repeated at the ordinary temperature, and after allowing the reaction mixture to stand for about 12 hours, only aniline (yield 9·2 g.) could be isolated. There was no trace of phenyl-hydroxylamine. The solution was faintly alkaline to litmus, and the odour of ammonia could be detected.

(*b*) *Triamido-phenol from Picric Acid.*—Picric acid on similar treatment to the above, at first gave picramic acid (yield 87%) and then triamido-phenol (yield 63 per cent.).

(*c*) *Benzhydrol from Benzophenone.*—Benzophenone was similarly treated in 75 % alcoholic solution with aluminium powder, and after about 12 hours a quantitative yield of benzhydrol was obtained in colourless crystals, m.p. 168°.

(*d*) *Aniline and Triaminobenzene from Chrysoidine.*—Chrysoidine on similar treatment gave an almost theoretical yield of a mixture of aniline and triamino-benzene (1 : 2 : 4).

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Alumina Gel as a Desulphurising Agent in Petroleum Refining.

By Jogendra Kumar Chowdhury and Ramesh Chandra Bagchi.

It is proposed to deal in this paper with the suitability of alumina gel for refining mineral oils containing sulphur compounds. The character and quantity of the sulphur compounds present in different oils vary according to the nature of the oil, certain American, Mexican and Persian mineral oils, brown coal and shale oils and cracked petroleum being particularly rich in sulphur compounds which not only cause colour and smell to the distillates but are largely responsible for corrosion, specially in internal combustion engines. Their removal is therefore a matter of importance for the refiner.*

Various methods, both chemical and physical in nature, are followed in large scale practice for the removal of these undesirable sulphur compounds. Treatment with concentrated sulphuric acid or with sodium plumbite, heating with certain metals or their oxides and in recent years oxidation with sodium hypochlorite may be mentioned as the more important chemical methods while washing with liquid sulphur dioxide (Edeleanu process) and selective adsorption by silica gel are the physical methods that are used on a large scale for desulphurisation of mineral oils. The chemical methods are either inefficient or destructive of some of the other constituents of the oil while the Edeleanu process demands special appliances and technical skill and is unsuitable when small amounts of sulphur compounds are the only ingredients to be removed. The use of suitable adsorbents for the purpose, however, appears promising, owing to the simplicity with which they can be applied to large scale practice and to the low concentration in which sulphur compounds occur in petroleum distillates; for, according to Freundlich's adsorption isotherm, the use of adsorbents will be more effective in dilute rather than in concentrated solutions.

* It has been estimated (Editorial Notes, *J. Ind. & Eng. Chem.*, 1927, **19**, 189)[1] that in U. S. A. 50 million dollars would be saved annually if petrol containing more than 0·1% sulphur could be used.

Various adsorbents have been tried by different workers for their specific adsorption capacity on sulphur compounds. The use of silica gel for desulphurisation has been studied by Waterman and Perquin (*Chem. Wok. Blatt.*, 1925, 378) and by Wood, Shelley and Trusty (*J. Ind. & Eng. Chem.*, 1926, **18**, 169) and since the war it has found increasing use in finely powdered or granular form as a desulphurising agent. The action of Fuller's earth and other naturally occurring or chemically activated silicates has been investigated by different authors and though they were efficient for removing colloidal dispersed materials, they were not found suitable for molecular dispersed substances. Activated carbon (Berl, *Zeit. ang. Chem.*, 1925, **39**, 428) has been found more suitable when water is used as solvent and its use with petroleum distillates has been further restricted owing to the difficulty of its regeneration. The suitability of bauxite for desulphurisation has been studied by Dunstan, Thole and Remfry (*J. Soc. Chem. Ind.*, 1924, **43**, 179T) and it has been found to be a good decolourising and desulphurising agent.

In view of the large deposits of bauxite in India, further study of its properties as adsorbent seemed desirable. To begin with pure alumina gel prepared in the laboratory was selected for investigation and its capacity of selective adsorption for different types of sulphur compounds dissolved in "shell motor spirit," from which low boiling fractions were distilled off, was determined. The necessity for distilling off the low boiling fractions arose from the fluctuations in the rate of burning with changes in room temperature while estimating sulphur by the lamp method and also from the risk of handling ordinary petrol in the laboratory. The solvent was found to be practically free from sulphur, containing not more than 0·002% of the ingredient.

The following substances were used as sulphur compounds: Dimethyl sulphate, tolyl mustard oil, ethyl mercaptan, methyl sulphide, allyl mustard oil and a mixture of all these compounds, this mixture being termed in the following experiments as "mixture of sulphur compounds." Alumina gel, the preparation of which is described later, was added to the sulphurous oil in dry condition, shaken for 15 minutes and filtered. The removal of sulphur was determined by estimations before and after treatment.

Estimation of Sulphur.—The usual lamp method with some modifications was used for the estimation of sulphur. The difficulty

of maintaining a constant rate of burning necessitated an arrangement (1) to adjust the size of the flame when necessary without any loss of the solvent and (2) to protect the wickholder from variations in temperature. This consisted in placing the wickholder inside another short piece of glass tubing supported on a piece of rubber tubing as in Fig. 1. This outer tubing served as a jacket protecting the wickholder from variations in temperature and could also be raised or lowered regulating the size of the flame in case of necessity, which however arose very rarely owing to the protection of the wickholder. This arrangement suited the purpose admirably, provided the head of the wick was kept sufficiently low inside its holder to prevent any oil accumulating in the jacket.*

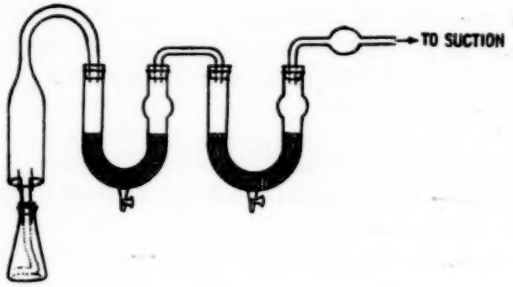


FIG. I.

About 3 gm. of oil were burnt in the course of a couple of hours in a 50 c.c. conical flask carrying a cork and a jacketed glass tubing to serve as a wickholder as described above. The wick-head was kept below the top of the wickholder, the flame being slightly bigger than the size of a pea. The products of combustion were drawn by suction through two **U**-tubes containing sodium bicarbonate solution of known strength, the suction arms being filled with glass beads and provided with bulbs. The excess of alkali was titrated with hydrochloric acid, using methyl orange as indicator. Concordant results were obtained provided the same wick was not used for too long a time.

Preparation and Activation of Alumina Gel.

Aluminium hydroxide was obtained as a flocculent gelatinous precipitate by slow addition of ammonia under vigorous stirring

* The suggestion for regulating the flame by means of a sliding tube has also been made by Squire (*J. Soc. Chem. Ind.*, 1926, **45**, 466T.)

to a solution of aluminium sulphate or chloride, the temperature not exceeding 25°. It was found by Yoe (*J. Am. Chem. Soc.*, 1924, **46**, 2390) that a high temperature of precipitation is detrimental to the adsorptive power of the gel. This was washed free from all impurities and was obtained in a hard glass-like form by slow drying in an air-oven at 60-70°, activated by ignition and consequent dehydration. As regards the suitable temperature of roasting, there is however no unanimity. Perry (*J. Phys. Chem.*, 1925, **29**, 1462) used a temperature of 200°, Munro and Johnson (*Ind. and. Eng. Chem.*, 1925, **17**, 88) activated alumina gel at 400°, Wood and others (*ibid*, 1926, **18**, 169) roasted at a temperature of 1000° while Dunstan and others (*J. Soc. Chem. Ind.*, 1924, **43**, 179T) recommend 600-700° for bauxite. In view of these contradicting reports it was found necessary to investigate the optimum temperature of roasting and water content of the gel with reference to sulphur compounds. The results are noted in the following table.

TABLE I.

Solution taken:—50 c.c. containing mixture of sulphur compounds.
Quantity of adsorbent—2 gms.; Size—20/50 mesh.
Temp. of treatment—25°; Time of shaking—15 mins.

Temp. of roasting °C	Water in the gel %	Adsorbent in 50 c.c. soln. gms.	Initial conc. of S, %	Final conc. of S, %	Removal of sulphur, %
75	44	2·3106	0·105	0·092	12·4
225-230	29	1·9408	,,	0·079	24·8
280-290	19	2·045	,,	0·071	32·4
350-400	6	2·1193	,,	0·069	34·3
Dull red heat	...	1·913	,,	0·074	29·5

In the above experiments the gel was heated for two hours to the required temperature in a paraffin-bath under slightly reduced pressure in a closed vessel to prevent contact with the fumes of the paraffin-bath and was cooled in a vacuum over P_2O_5 before use. It will be observed from the above table that the adsorption capacity rapidly increases with dehydration until the moisture content is 19 %, further increase with dehydration being very slow, while too high a temperature is unfavourable. It is evident that the gel must be dry enough to have the capillary pores and the surface energy free but too drastic a drying would affect the structure of the gel and the size of the pores.

The unfavourable effect of high temperature of roasting has also been observed with other adsorbents. Ruff (*Chem. Zent.*, 1926, I, 1781, 2657, 2306,605) has shown that the decrease in adsorption capacity of activated carbon by heating above 1000° is due to its slowly being converted into crystalline form. Kyropoulose (*Chem. Zent.*, 1917, II, 450) and Braesco (*Chem. Zent.*, 1919, I, 906) have shown that silica gel is partly converted into crystalline form by heating or standing for a long time. In case of alumina gel a similar transformation coupled with the collapse of the pores at too high a temperature is a probable explanation for its reduced activity.

Optimum Conditions for Desulphurisation.

A study of the optimum conditions to secure maximum desulphurisation by means of alumina gel as prepared above was then undertaken. It is well known that adsorption is influenced by various factors, namely, character and concentration of the sulphur compounds, quantity and size of particles of the adsorbent and temperature of treatment. The following experiments are therefore intended to find out the best conditions under which alumina gel should be allowed to act.

(*a*) *Concentration of Sulphur Compounds.*

As is to be expected from Freundlich's equation the percentages of sulphur compounds removed increase with dilution. That the process involved is essentially one of true adsorption may also be deduced from this application of Freundlich's equation:

$$\frac{x}{m} = Kc^{\frac{1}{n}}$$

where x/m = quantity adsorbed per gram of adsorbent ;

c = concentration of the solution in equilibrium with the adsorbed substance;

K and n are constants, n being greater than 1.

By plotting x/m against C, a curve of the nature of a parabola as shown in Fig. II is obtained.

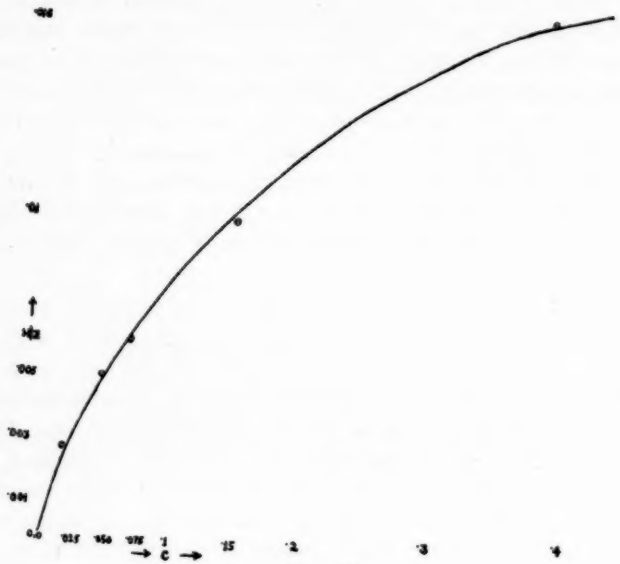
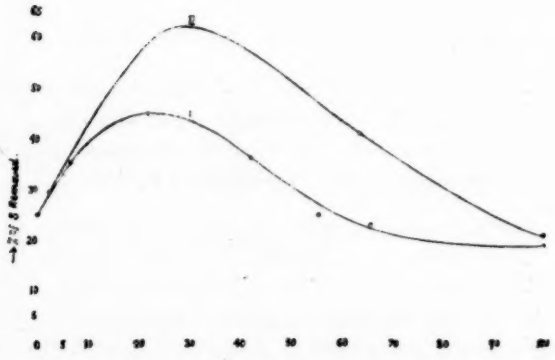


FIG. II.



→% *of carbon or silica in the mixture.* FIG. III.

I. Curve for the mixture of alumina and carbon.
II. Curve for the mixture of alumina and silica.

Taking the logarithms, the equation becomes

$$\log \frac{x}{m} = \frac{1}{n} \log c + \log K$$

In this form a straight line may be obtained by plotting log x/m against log c.

The results obtained with variation in concentration are given in the following table.

TABLE II.

Solution taken :—40 c.c. containing methyl sulphide.
Adsorbent used :—4 gms., 50—160 mesh, at 25°C.
Time of shaking :—15 mins.

Initial conc. of S, %	Adsorbent gms.	Final conc. of S, %	Removal of S, %	x/m	log x/m	log c.
0·452	4·15	0·385	14·8	0·0161	−1·7932	−0·4145
0·179	3·20	0·148	17·5	0·0097	−2·0132	−0·8297
0·091	3·85	0·068	25·2	0·006	−2·2218	−1·1675
0·069	4·7	0·046	33·3	0·0049	−2·3098	−1·3372
0·026	3·3	0·017	34·6	0·0027	−2·5686	−1·7696

TABLE III.

Conditions same as in Table II, but with different sulphur compounds.

Sulphur compounds.	Initial conc %	Final conc. %	Removal of sulphur, %
Benzyl mercaptan	0·443	0·397	10·6
	0·125	0·105	16·0
	0·081	0·056	30·0
Allyl mustard oil	0·291	0·245	15·8
	0·130	0·102	21·5
Tolyl mustard oil	0·165	0·136	17·6
	0·059	0·036	38·9

(*b*) *Quantity of the Adsorbent.*

It will be seen from the following table that the percentage of sulphur removal increases with the quantity of adsorbent used. But the fact that a considerable amount of the solvent is adsorbed and also held mechanically by the adsorbent makes it desirable that its use should be limited to the lowest effective amount.

TABLE IV.

Sulphur compound used :—Tolyl mustard oil.
Other conditions same as in previous table.

Quanatity of adsorbent in 40 c.c. in gms.	Initial conc. of S, %	Final conc. of S, %	Removal of S, %
0·98	0·087	0·084	... ...
3·2	,,	0·074	15
13	,,	0·04	54

(c) *Size of Particles.*

It has been found that silica gel in granular form as prepared by Maschinenfabrik Fr. Herrmann, G.m.b.H. (Germany) is particularly suitable for use as adsorbent (Koetschan, *Zeit. ang. Chem.*, 1926, **40**, 210). In the case of alumina gel 50/160 mesh is found to be the most suitable size as will be seen from the following table. It is likely that the size of the pores are affected when very finely powdered though a larger surface thereby becomes available. The size of the particles will naturally influence the choice of the method of filtration, the large particles being more suitable for column filtration and regeneration by means of steam and air while finely powdered adsorbent has to be stirred with the oil with subsequent filtration and regeneration by means of extraction with solvents. The loss due to dust formation is also considerable.

TABLE V.

Sulphur compound:—Tolyl mustard oil.
Adsorbent:—2·8 gms. in 40 c.c. solution.
Temperature and time of shaking same as before.

Size of particles, mesh per sq. in.	Adsorbent per 40 c.c., gm.	Initial conc. of S, %	Final conc. of S, %	Removal of S, %
10-20	2·76	0·087	0·073	16·1
20-50	2·75	,,	0·071	18·4
50-160	2·65	,,	0·069	20·7
less than 160 mesh	3·2	,,	0·074	15·0

(d) *Temperature of Treatment.*

It will be observed from the following table that a high temperature favours desulphurisation though this is contrary to the usual gaseous adsorption phenomenon. Increased desulphurisation with rise of temperature has also been observed by Dunstan, Thole and Remfry (*J. Soc. Chem. Ind.*, 1924, **43**, 179T) in the case of bauxite. According to them, polymerisation and in some cases partial decomposition takes place, specially at a high temperature and the products are then more easily removed by adsorption.

TABLE VI.

Sulphur compound :—Tolyl mustard oil.
Size of particles :—20/50 mesh.
Other conditions same as before.

Solvent.	Adsorbent in gms.	Temp. of treatment. °c	Time of contact (mins.)	Initial conc. of S, %	Final conc.	Removal of S, %
Petrol	2·76	25·0	15	0·072	0·058	19·4
,,	2·23	100	60	,,	0·05	30·6
Kerosene	2·5	25	15	0·083	0·068	18·1
,,	2·62	140	60	,,	0·055	33·7

(e) Types of Sulphur Compounds.

The following table indicates the power of selective absorption of alumina gel for different types of sulphur derivatives. The remarkably high adsorption of dimethyl sulphate (75%) even in fairly concentrated solution indicates that here the basic nature of the adsorbent comes into play. A neutral adsorbent, activated carbon (Kahlbaum) was tried on dimethyl sulphate under the same conditions as with alumina and showed only 25·7% S-removal.

TABLE VII.

Sulphur compounds.	Initial conc. %	Final conc. %	Removal %
Dimethyl sulphate	0·266	0·066	75
Tolyl mustard oil	0·0585	0·036	38·5
Hydrogen sulphide	0·08	0·068	15
Benzyl mercaptan	0·0814	0·0565	30·6
Methyl sulphide	0·0914	0·0675	26·2
Allyl mustard oil	0·13	0·102	21·5
Ethyl mercaptan	0·051	0·04	21
Elementary sulphur	0·097	0·098	...
Carbon Disulphide	0·098	0·098	...
Phenyl mustard oil	0·14	0·129	7·8
Mixture of S-compounds	0·105	0·079	24·8

Note :—The concentration of the S-compounds should be borne in mind while comparing the results given in the last column.

Catalytic Oxidation of Sulphur Compounds with Atmospheric Air.

The high percentage of removal in the case of dimethyl sulphate led to the following attempts for the oxidation of sulphur compounds before adsorption. As already mentioned, sulphur compounds are now oxidised on a large scale by means of sodium hypochlorite and are removed by subsequent washing and adsorption. The preparation of a reagent of suitable alkalinity and available chlorine, the susceptibility of other constituents of the oil to the action of chlorine as also economic consideration suggest, if possible, the use of atmospheric air in place of the chemical reagent. In the following experiments, oxidation has been carried out by means of atmospheric air using alumina gel as a catalyser.

Alumina is known as a useful catalyser in many gas reactions such as oxidation of hydrogen sulphide, dehydration of alcohols and some other reactions. Badische Anilin und Soda Fabrik (D. R. P., 405850) used alumina gel as a catalyser in the liquid phase for the oxidation of higher petroleum hydrocarbons. This is one of very few instances where alumina is used as a catalyser in liquid phase. When sulphur compounds are dissolved in petroleum, they resist oxidation with atmospheric air, being protected by surrounding hydrocarbons. Alumina gel however adsorbs the sulphur compounds on its surface and when atmospheric air is passed through makes direct contact with oxygen possible, thus facilitating the oxidation of the sulphur compounds.

The following experimental procedure was adopted:—The oil containing different S-compounds was taken in a round-bottomed flask and heated to about 150° in an oil-bath under reflux using two spiral condensors circulated with ice-cold water to prevent loss of the solvent due to evaporation, while air freed from carbon dioxide and moisture was passed through the heated oil for about a couple of hours at the rate of 20 litres per hour, about 4 gm. of alumina being used for every 50 c.c. of the oil. Owing to the loss of the solvent, it was necessary to conduct blank experiments under same conditions but without the use of any alumina in order to get a correct idea of the catalytic action of the gel. The oil was then cooled and filtered and the amount of S-removal ascertained. In order to see if the hydrocarbons of the solvent were also oxidised by the above treatment, they were shaken with dilute alkali in a stoppered burette but no diminution in volume was detected. It may therefore be assumed that the solvent remains practically unaffected by the treatment. The results are shown in Table VIII.

TABLE VIII.

Experiment.	S-compounds.	Alumina in 50 c.c. (gm.)	Rate of air blowing, litres per hr.	Time of treatment (mins.)	Temp. of treatment °C.	Initial conc. of S, %	Final conc. of S, %	Removal of S, %
Without alumina	Benzyl mercaptan	0	20	90	160	0·085	0·104	...
With alumina	,,	4	,,	,,	,,	,,	0·032	69·2
Without ,,	,,	0	15	150	150	0·284	0·319	...
With ,,	,,	4	,,	,,	,,	,,	0·130	59·2
Without ,,	Free S	0	20	90	140	0·120	0·137	...
With ,,	,,	4	,,	,,	,,	,,	0·065	52·5
Without ,,	Mixture of S-compounds	0	,,	,,	175	0·105	0·071	32·4
With ,,	,,	4·5	,,	,,	,,	,,	0·016	77·5
Without ,,	Carbon-disulphide	0	,,	,,	160	0·092	0·038	58·7
With ,,	Phenyl mustard oil	4	,,	120	180	0·140	0·035	75·0

Note :—The concentration of S-compounds after passing air without the addition of alumina is taken as real initial concentration when calculating the percentage of S-removal with alumina as catalyser.

The results shown in this table are not however strictly comparable owing to variations in concentration and other factors. It will be noted that 60-80% of different S-compounds, depending on initial concentration and other factors, was removed by this treatment. These figures compare favourably with those obtained by sodium hypochlorite treatment (Birch and Norris, *J. Chem. Soc.*, 1925, **127**, 1934 ; Wood and others, *J. Ind. & Eng. Chem.*, 1926, **18**). Elementary sulphur which is practically unaffected by the use of the adsorbent alone is removed to the extent of 52·5% in the course of one and a half hour. A comparison with Table VII will show a general increase in desulphurisation. If the solvent lost during the treatment be recovered, the process appears capable of large scale application, specially with those mineral oils which are poor in olefinic and other easily oxidisable hydrocarbons.

Effect of Mixtures of Alumina Gel with other Adsorbents.

It is well known that the presence of certain substances remarkably promotes the activity of catalysers and as a consequence mixtures are being increasingly used for catalysis, but instances of the use of mixtures for adsorption are very rare. Reyerson (*J. Phys. Chem.*, 1927, **31**, 88) observes that gases are better adsorbed by silica gel in the presence of very finely divided metals than by the gel alone. Fells and Firth (*J. Soc. Chem. Ind.*, 1927, **41**, 39T) state that slightly increased adsorption of benzene and toluene takes place when an intimate mixture of silica gel and carbon (from cane sugar) is used as absorbent. Increased effect of silicalised carbon has also been observed by Berl (*loc. cit.*) though no figures are given to indicate the amount of increase. The German Patent No. 402488 mentions that a mixture of iron hydroxide with carbon effectively destroys the corrosive action of coal-distillates.

(*a*) *Mixture of Alumina Gel with Activated Carbon.*

Preparation.—An intimate mixture was obtained by suspending finely divided activated carbon (Kahlbaum) in a solution of aluminium sulphate and then precipitating the hydroxide by the addition of ammonia, drop by drop with constant stirring, the temperature not exceeding 25°. This was washed free from all impurities and after preliminary drying at 60°-70° it was obtained in the form of a hard glassy mass. This was powdered to 20/40 mesh, heated to 230°-235° for two hours and cooled in a desiccator before use.

The amount of carbon in the gel was approximately determined by ignition, the water content of the alumina dried at 230° being taken at 29% (Table I).

The results obtained with different percentages of activated carbon are shown in the following table. It will be observed that maximum efficiency is obtained with 21·7 % of carbon in the gel, the sulphur removed being 44·8 % against 24·7 % with pure alumina gel and 18·2 % with activated carbon.

TABLE IX.

S-compound :—Mixture of sulphur compounds.
Size :—40/50 mesh ; 2·4 gms. for 25 c.c. solution.
Time and temperature as usual.

% Carbon in adsorbent.	Quantity of adsorbent (gm.)	Initial conc. of S, %	Final conc. of S, %	Removal of S, %
0	2·4	0·105	0·079	24·7
6·5	2·4	,,	0·068	35·2
21·7	2·38	,,	0·058	44·8
42 4	2·41	,,	0·067	36·2
55·8	2·4	,,	0·079	24·7
66	2·39	,,	0·081	22·8
100	2·38	,,	0·086	18·1

(*b*) *Mixture of Alumina and Silica Gels.*

Preparation.—Silica gel was obtained by slowly adding hydrochloric acid to a solution of sodium silicate and washing free from impurities. This gel was suspended in a solution of aluminium sulphate and under constant stirring aluminium hydroxide was precipitated by slow addition of ammonia. This was dried as before first at 60°-70° and subsequently at 230°-235° for two hours. The percentage of silica in the mixture was determined gravimetrically after washing off the alumina with warm dilute nitric acid. The results obtained with different percentages of alumina and silica are shown in the following table.

TABLE X.

Conditions same as in previous table.

% Silica in the mixture.	Gms. adsorbent in 25 c.c.	Initial conc. of S, %	Final conc. of S, %	Removal of S, %
0·0	2·11	0·117	0·088	24·8
2·4	1·98	,,	0· 83	29·1
23·7	2·05	,,	0·047	60·0
63·7	2·12	,,	0·070	40·2
100	1·95	,,	0·094	20·0

It will be observed that the mixture with 23·7 % of silica adsorbs 60 % of S-compounds while the figures for pure alumina and silica gels are only 24·8 % and 20 % respectively. This enormous increase in the adsorption capacity does not seem to be due to any increase in surface area caused by precipitation of alumina on finely divided substances. Mixtures obtained by precipitating alumina on comparatively inert substances such as powdered glass or pumice stone, however, showed no increased adsorption capacity. This must therefore be attributed to the combination of pores of different sizes in the mixture. Further work in this line is being continued.

Regeneration of the Adsorbent.

The method of regenerating adsorbents by means of super-heated steam and air is also suitable in the case of alumina gel as will be evident from the following table. Inspite of the basic nature of the gel, it does not apparently suffer any permanent reduction in its adsorption capacity and may be restored to almost its original activity.

TABLE XI.

Adsorbent:—Alumina gel used in previous experiments, 2 gm. for 25 c.c. solution.
S-compound :—Mixture of sulphur compounds.
Other conditions as usual.

Treatment of the adsorbent.	Initial S, %	Final S, %	Removal of S,%
Passed steam for two hrs. at 200° activated in paraffin-bath at 239° ...	0·105	0·086	18·1
Passed steam at 230° for 1/2 hr. then air at 230° for 1/2 hr. and again steam at 230° for the same period and finally activated at 230° for two hours. ...	,,	0·078	25·7
Freshly prepared alumina activated at 230° for two hours. ...	,,	0·079	24·8

In conclusion, it may be pointed out that the figures for desulphurisation given in the above tables are by no means the maximum attainable but depend on the quantity of the adsorbent used, concentration of S-compounds as well as on other factors. In column filtration, for example, the first fractions will be free from sulphur, the amount of which will however increase as the filtration proceeds.

Summary.

1. Sulphur in the oil has been estimated by the lamp method which has been suitably modified to give concordant results.

2. Optimum conditions for the activation of alumina gel, *i.e*, the temperature of roasting and moisture content have been determined. Influence of other factors such as concentration and nature of S-compounds in the oil, quantity and size of particles of the adsorbent and temperature of treatment on adsorption has also been ascertained. Freundlich's adsorption isotherm has been found satisfactorily applicable.

3. Most of the sulphur compounds used have been satisfactorily removed by oxidation with atmospheric air, using alumina gel as a catalyser and subsequent filtration. This is an improvement on the present process of oxidation with sodium hypochlorite used on a large scale.

4. It has also been found that intimate mixtures of alumina gel with other adsorbents such as activated carbon or silica gel, specially the latter, mutually promote the adsorption capacity to a remarkable extent. This is similar to the action of promoters used in the preparation of catalysts.

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Chemistry in the Service of India.

By Gilbert J. Fowler, D.Sc., F.I.C.

President, Indian Chemical Society.

Let me in the first place express my very sincere appreciation of your kindness in unanimously electing me President of the Indian Chemical Society. I feel it to be an honour to succeed so distinguished a predecessor as Sir P. C. Rây, more especially since I can not claim to be one of those who in the words of an American technical chemist, "daily sup with electrons." When such matters as atomic constitution and Werner's theory of co-ordination are under discussion I keep discreetly silent, when the organic chemist not content even with what some of us irreverently term "wire-netting" goes on to describe cage formulae and spiro-compounds I listen with all respect. Nevertheless I have a shrewd suspicion that there are others in my case and I take comfort in the fact that there are large areas of chemical knowledge, especially those concerned with the application of chemistry to the uses of life, which are still within the reach of ordinary mortals. We have to bear in mind that the phenomena of chemistry remain the same though theories develop. It may be doubted whether the extensive knowledge of facts, and diversity of phraseology possessed by the modern student really imply a clearer concept of the colloid state than was possessed by Graham.

It is necessary that we should not confuse knowledge about things with knowledge of the things themselves. It has been suggested by a modern witty philosopher of a more solemn writer, world famous in his day, that had he once encountered a live fact he would have fled screaming. On the other hand the discoverer whose genius more than any other has influenced the externals of our modern life, Michael Faraday, was, I believe, innocent of mathematics, though his clear vision of essentials enabled his theories to be put into mathematical form by Clarke Maxwell.

The bearing of these observations on the subject of my address "Chemistry in the Service of India" will be seen if I mention the

following facts. At the Benares meeting of the Indian Science Congress a discourse was given on the structure of the atom and the large hall of the University was filled. At a symposium on the subject of the true path of Indian industrial development the audience was scarcely more than 20 individuals. In the U. S. A. on the other hand a 20 million dollar fund has been supported by Secretary Hoover to encourage students to take up purely scientific studies at the University, lest the stream of fundamental knowledge should dry up at its source.

In the U. S. A. we hear that the workman drives to his work in a Ford motor car. In India untold millions eke out a bare living on the verge of starvation. This poverty trouble is not confined to tillers of the soil, the difficulties of the Indian middle class are well known. Only a short time ago I was criticising, perhaps a little severely, what seemed to be lack of initiative and originality of thought on the part of an M.A. graduate, and he replied "I am afraid, we are so concerned with merely getting a living that we have no time to think."

How can chemistry help us in the solution of this problem and how in the solution of it can Indian chemists help themselves, is the subject which I desire that we should consider to-day. At this point I should like to emphasise, what has been so well put by Sir P. C. Rây in his note to the report of the Thorpe Commission on the projected Chemical Service, that chemistry in the service of India does not necessarily mean the same thing as Indians in the Chemical Service. Until an increasing number of Indian students of Chemistry are able to earn a living outside of appointments under Government or of subordinate positions in large business concerns, the problem will not be solved nor will chemical science be really applied to the service of this country in any effective way. Moreover, year by year, more and more young students of chemistry are being turned out from the increasing numbers of Universities and Technical Institutes. All of these cannot expect to find Government posts, and already warning voices have been heard from the commercial world that existing mills and factories are nearing saturation point so far as the employment of chemists is concerned. Moreover many of those who are employed cannot be termed anything more than analysts whose prospects are necessarily limited. On the other hand those of a wide training who can really claim to be technical chemists, or at any rate would become such if given

the opportunity, have great difficulty in obtaining suitable employment. Some specially brilliant men have to my great regret forsaken the profession for lucrative employment elsewhere. To arrive at some remedy for this state of affairs we may perhaps usefully consider the situation systematically under the following heads:—

1. Industrial Conditions in India.
2. Chemical Education in India.
3. Existing Outlets for Chemical Students.
4. Future Developments.

1. *Industrial Conditions in India.*

We have to bear constantly in mind the fact that industries, nearly always, have begun as arts, and it is only after a certain stage of development has been reached that the assistance of advanced science is called for.

I myself remember the early days of metallography when under the enthusiastic guidance of Professor Arnold of Sheffield I laboriously polished my sections of iron and steel. Since then this science has been applied to the whole vast industry of special steels and alloys of every description, and in an industrially developed country affords employment for many specially trained men. Outside of Jamshedpur, how many such openings are there in India?

Nevertheless excellent steel was made in Sheffield before the advent of the microscope, mainly because a large population of workers had grown up in whom the knowledge of iron and steel production and working was inbred. It has been for the research chemist to find out by prolonged investigation what the workman means who examines the fracture of a test piece of steel and says there is no 'nature' in it.

Until the chemist is able not only to give scientific descriptions, but also to be responsible for the actual control of a technical process, the possibly illiterate workman, who can actually do things, is the more valuable individual.

I have taken this one example with which I happen to be familiar. Many others may be cited. How many chemists does the textile industry of India support, other than occasional analysts of accessory material such as size, fillers, etc.? We may hope the work of the

Indian Cotton Committee will show the way to extended application of scientific knowledge.

Hides are tanned, lac is grown and manufactured, oil is pressed with little assistance from the chemist. In all these cases I do not for a moment suggest that there is not abundant scope for the application of chemical science, my point simply is that the industries come into existence and carry on at any rate to some profit before thinking about chemists, therefore the chemist has to *prove* his value to the manufacturer.

At this point we must distinguish between a chemist and an analyst. The general public unfortunately has little conception of what the work of a chemist really is, like the steel works manager of old days about whom Professor Arnold told me, who strolled into the laboratory and remarked " 'eres where you does your tests I suppose does 'em wi' drugs I reckon," and who referred to the future scientific leader of the iron and steel industry as " that there chemical."

I have found the best way to bring home the difference between a chemist and a " tester " or " analyser " is to contrast a draughtsman with an engineer. An engineer must be a good draughtsman but a draughtsman is not necessarily an engineer, *i.e.*, he is not primarily responsible for design. As an engineer is one who thinks in terms of engineering so a real chemist is one who " thinks chemically." A technical chemist must even go further and think in terms of technical possibilities, he must possess what I once ventured to describe as " technical sense."

It is now just 10 years ago since I used that expression in my Presidential Address to the Chemical Section of the Indian Science Congress at Lahore and it is of interest to see what the experience of these 10 years has taught.

I am just as certain as ever that no serious progress can be made in the application of science to industry in the absence of men who possess this technical sense. On the other hand it has become clear that the development in India of large scale manufacturing industries, requiring the services of such men will be at a much slower rate than was at one time thought likely owing largely to the absence of an industrial population such as I have referred to in the case, *e.g.*, of Sheffield.

Quite recently I was discussing the possibility of starting a glass factory at a certain locality and the fundamental condition which

made it possible at all was the presence of a number of indigenous glass blowers in the neighbourhood. The glass factory had to be based primarily on their aptitude.

I feel therefore that the industrialisation of India must come gradually by careful utilisation of the material to our hand.

The material we are primarily concerned with is the Indian chemist which brings us to our second matter for consideration, *viz.*

2. *Chemical Education in India.*

Speaking in Calcutta there is no temptation to question the ability of Indians to carry out scientific research of the highest order, it is sufficient to mention the names of Bose, Rây and Raman. In our *Journal* which I have studied with some care there are contributions which seem to me to be of great value from such workers as Bhatnagar, Ghosh, Mukherjee and B. K. Singh, to mention only a few out of many others, there is therefore small likelihood of the torch of pure scientific inquiry being extinguished in India.

In bio-chemistry, with which I am more familiar I am proud to name among my own students several who have shown themselves more than able to hold their own in competition with workers of their own status in England. Even in purely technological activity, the results of which do not find publication in the ordinary journals, I know of many Indians who are doing excellent work.

All these however are outstanding men, and we have to consider the rank and file, and it is here that the question of education becomes of first importance. I have recently had occasion to interview a number of candidates for admission to courses in technological chemistry, and I have been very much concerned to find how little real knowledge of chemistry is possessed by the ordinary pass B.Sc. Information apparently has been merely swallowed, not assimilated. Too often the candidate complains that it is several months since he passed his examination, therefore he cannot be expected to remember quite simple chemical facts. There appears to be almost complete ignorance of what may be called general knowledge, involving chemical information, such for instance as the composition of glass or pottery, the simple chemistry of plant growth, or the sources of India's coal supply.

It is disconcerting to have to interrupt a lecture to science graduates in order to fill in lacunae in " general knowledge." Chemistry

which is only a matter of memorising formulae and equations is a dead thing of no cultural or vocational value. What is the use of knowing that the formula of potash is KOH if it calls up no mental picture of the actual substance and its properties.

I feel strongly that the whole programme of the teaching of science in our schools and colleges needs revision in the direction of a greater sense of reality. What is required is something of the nature of what used to be called " natural philosophy " which might be defined as the illustration of scientific principles from the world we live in. Such a course was to be found in an excellent handbook for French schools by Paul Bert in which were given in most interesting fashion, with copious illustrations, the elements of botany, zoology, geology, physics and only finally chemistry.

The other day, however, I was glad to learn from an officer in the United Provinces Educational Service that a course of science is to be introduced in the vernacular schools in the U. P., and that in the high schools the concept of science teaching is to be extended along the lines suggested.

Much freer use should be made, I would suggest, of *viva voce* methods in examination.

In this respect the examinations of the Institute of Chemistry, which are designed to discover whether a candidate is a live chemist or only a memoriser, may perform a valuable function now that the examination can be held in India, and every encouragement should be given to students to qualify for the Associateship Examinations.

A sound basis of scientific principles both physical and chemical must precede anything in the nature of advanced technical training, there must in fact be some science present before it can be applied.

This next stage of training, *viz.*, the technical application of scientific principles, is not so easy to arrange for. Just as it is necessary to have some science to apply, so there must be knowledge of practice to which to apply the science, and it is here that the difficulty arises.

In the very frank and valuable address of Sir William Marris at the opening of the recent industrial exhibition in Lucknow he states what we must recognise to be the fact that until we can ourselves carry out a technical process to profit we are only amateurs. No amount of training in the shelter of a Polytechnic or as a temporary apprentice in a works can give that reality of knowledge that comes from experience of actual financial responsibility.

Unfortunately those who are in a position to bring such experience to the service of teaching are often doing better by carrying on their actual business than they could by imparting their knowledge to others. Moreover a first rate technical expert may not equally have the gift of imparting to others the results of his experience.

So we are in danger of a vicious circle, the specially trained student begins to teach before he has proved his ability commercially, his students teach other students and so the original knowledge derived from works experience becomes sadly diluted.

The only way that I see out of this dilemma is that the remuneration for such teaching either by way of salary, or freedom for private practice should be adequate to attract men with real practical experience.

This method is more and more in vogue in Municipal service in England and has been always recognised in the University teaching of Medicine and Law.

3. *Existing Outlets for Chemical Students.*

Granted we have well trained students the problem is still what to do with them. The question may be asked whether in the present state of Indian industry such students can find satisfactory employment. In my judgment, given the requisite product of the training which I have indicated, there should be no difficulty in finding modest outlets for the employment of chemists for some time to come along existing lines. It is encouraging to find from statistics in my possession that although the proportion of chemical students turning to teaching or Government service is still high, there is a distinct increase of late years in the number of those engaged in connection with manufacturing industry. A number of manufacturing concerns have recently employed a trained chemist for the first time and have found that he has more than earned his salary.

Moreover, Government, Railway and Muncipal services are finding new work for chemists in connection with such matters as milk and food protection, water supply and sewage purification, and stores control.

There is a large opening for scientifically trained commercial travellers to develop demand for the products of chemical and kindred industries. The extraordinary success of the advertising campaign of the Tea-Planters' Association should stimulate like enterprise in other directions.

I look for a great increase in chemical work in connection with agriculture as soon as the Royal Commission has reported.

More and more it is becoming evident that modern agriculture is a branch of bio-chemistry. The recent work at Rothamsted, Bangalore and Cawnpore on the preparation of artificial farmyard manure opens up quite new possibilities in the application of bio-chemical forces.

The fascinating researches on scientific manuring now in progress at Coimbatore in conjunction with the experiments on animal nutrition at Coonoor have shown the extraordinary influence on the fertility and nutritive value of the seed of the application to the crop of comparatively small amounts of nitrogenous organic matter, while small variations in the mineral constituents of the plant food have been shown greatly to influence the character of the plant products. These results corroborate kindred work at Bangalore on the influence of various fertiliser elements on the growth of the host plants of lac, with consequent effect on the yield and character of the lac produced.

All these, and many other developments of biochemical research indicate that large additions should be made to the research staff of the agricultural departments if the premier industry of India is to reap the fullest benefit of modern discovery.

4. *Future Developments.*

In the above directions, therefore, are to be found an increasing number of "jobs" for chemists. As was stated at the outset however our efforts to give to India the best service of which chemical science is capable will largely fail unless the rank and file of our chemical students are imbued with the spirit of "creative enterprise" which, to again quote Sir William Marris, is essential for true industrial progress. Every man who can start a paying industry and carry it on of his own initiative is doing the very finest service to his country, as well as building up a happy and independent career for himself. Here will be the test of the reality of the training which our schools and colleges can give, not necessarily a training sufficient to qualify for immediate financial responsibility in industry but at any rate a training in essentials and in the acquirement of the right attitude of mind. It has been said that the young subaltern on receiving his commission is not expected to perform the duties of a general or to be able to devise schemes of strategy and tactics

but at least he should be able to deliver a squad of men at a given place punctually at a given time.

It is this quality of trustworthiness that almost more than anything else is required of the budding industrialist. If he is preparing only a single material let it be always of the quality specified, and always delivered on time. Even in the manufacture of such apparently simple household things as jams or jellies his training, if it has been satisfactory, should enable him to maintain always the same taste and quality, proper keeping properties, neat make up and adequate stock in hand.

I am happy to know that quite a number of chemical students are making their own industrial ventures with success. At the Harcourt Butler Technological Institute the endeavour is being made to ease the initial anxiety of such enterprises by allowing ex-students to make use of the large scale plant at the Institute to prepare soap, express oil or tan hides from their own raw materials, charging a fair price for such service.

It is often queried how can such small ventures compete with modern large concerns. The answer is, because they are small and the overhead charges are correspondingly trifling.

Many world-famous products have originated in back kitchens of small shops. Such I believe was the birth place of McKintosh's toffee and of Crawford's biscuits. Others such as Lazenby's sauce are still made as I have myself seen, in a small room of a big factory.

There is no essential reason therefore why such small factories should not be the precursors in India of real indigenous industries on modern lines.

Especially does this apply to agricultural industries of which much has already been written. The most recent suggestion is the production of egg powder, an industry largely dependent on imports from China which have now greatly diminished owing to the disturbed state of that country. More and more the chemist should help to convert the struggling farm into a flourishing "food factory." Then we shall see realised the fine ideal urged by Lord Irwin of the "scholar ploughman."

It should be the aim of the true agricultural industrialist to economise his forces and machinery as carefully on his farm as the works manager in purely chemical industry.

Some remarkable articles have recently appeared in the valuable little paper edited by Captain J. W. Petavel, known as "Bread and

Freedom," the organ of the movement for dealing with the poverty problem on the lines advocated by that great son of Bengal, Sir Asutosh Mookerjee.

Attention is drawn in these articles to the enormously increased crop yields obtained by the intensive trituration of soil and the transplantation of seedlings by recently invented special machinery, thus indicating the possibilities of a "technified" agriculture.

To illustrate the increase in crop yield which may be obtained if thorough scientific control is exercised, I may perhaps usefully mention an instance within my own experience. Knowing that tomatoes grew like weeds in Nasik and that I could only get 4 annas for a mali basketful in the bazaar, I suggested to a large firm in England the possibility of providing bulk canned tomatoes from India rather than from the United States. I went carefully into costs using very cheap labour and outfit and forwarded a price to London. I was told that I must halve my price per ton before I could compete. The labour and outfit costs could not be reduced, the freight was not excessive, where then was the snag? It appeared that the utmost crop which had so far been raised in Nasik was 9 tons per acre. On consulting the Report of the Intelligence Department of the Ministry of Agriculture and Fisheries, London, I found that at the Research Station at Waltham Cross a yield of 50 tons of tomatoes per acre had been obtained by the use of thoroughly rotted turf as a manure.

A case is reported in Farmer's Bulletin No. 133 of the U. S. Department of Agriculture where under the best conditions a tomato crop worth Rs. 18,000 has been sold from one acre during a season.

Facts such as these and many others which might be cited, make it clear that if anything like the scientific study and capital outlay was bestowed on agricultural industry, as is given to what may be termed "mechanical" industry, marvellous results would be obtained. The law of diminishing returns would seem, in the light of modern researches, to be much less forbidding than was at one time supposed.

I would urge that here the Indian chemist has an unlimited field for his energies. It seems impossible to conceive that such fascinating work, could for a moment be deemed derogatory to social dignity. Unintelligent monotonous toil may be felt to be unworthy of so called educated people but such work as is possible to the "scholar ploughman" is the most engrossing that can well be conceived, besides

affording possibilities of great increase of material wealth to the individual, to those associated with him and ultimately to the whole country.

In the various directions indicated in the foregoing discourse, I have tried to show the great possibilities of Chemistry in the service of India. In this service there is ample scope for that true patriotism which finds its expression through productive work rather than by emotional rhetoric.*

* Presidential address delivered at the Annual General Meeting of the Indian Chemical Society, Calcutta, on 6th January, 1928.

Varying Valency of Platinum with Respect to Mercaptanic Radicles. Part VII.

By Prafulla Chandra Rây, Kshitish Chandra Bose-Rây and Sachindranath Ray-Chaudhury.

Many complex compounds derived from chloroplatinic acid and various organic thio-compounds (mercaptans, sulphides, disulphides etc.) have already been described (Rây, *J. Chem. Soc.*, 1919, **115**, 872; Rây, *ibid.*, 1922, **121**, 1283; Rây, *ibid*, 1923, **123**, 133; Rây and Bose-Rây, *J. Indian Chem. Soc.*, 1925, **2**, 178). The action of various bases on some of these complex bodies to elucidate their constitutions has also been investigated (Rây, Guha and Bose-Rây, *J. Indian Chem. Soc.*, 1926, **3**, 155; Rây, Guha and Bose-Rây, *ibid.*, 1926, **3**, 358; Rây, Bose-Rây and Adhikari, *ibid*, 1927, **4**, 467).

In the present work, the action of another organic thio-compound, benzyl sulphide, on chloroplatinic acid has been studied and the compounds (1) $PtCl_3 \cdot 2Bz_2S$* and (2) $PtCl_2 \cdot 2Bz_2S$ (also a molecular compound of the above two, $Pt_2Cl_5 \cdot 4Bz_2S$) have been obtained.

These two compounds have then been subjected to the action of bases like ammonia, pyridine, etc., and a study of the resulting products has been found to throw considerable light on the constitution of the parent bodies (*cf.* Rây, Guha and Bose-Rây, *J. Indian Chem. Soc.*, 1926, **3**, 155; Ray, Bose-Rây and Adhikari, *ibid.*, 1927, **3**, 467). The products are mostly compounds of the Werner type, which directly suggests that the compounds (1) and (2) themselves possess Werner constitutions.

Constitution of $PtCl_3 \cdot 2Bz_2S$.

Molecular weight determination in naphthalene by the freezing-point method corresponds to the single formula. Hence it cannot be a molecular compound of $PtCl_4 \cdot 2Bz_2S$ and $PtCl_2 \cdot 2Bz_2S$ (*cf.* the formula of $PtCl_3 \cdot 2Et_2S$: Rây and Bose-Rây, *J. Indian Chem. Soc.*, 1925, **2**, 178; Rây, Guha and Bose-Rây, *ibid.*, 1926, **3**, 155) or possess the formula $[Pt(Bz_2S)_4] \cdot PtCl_6$ (*cf.* the formula for $PtCl_2 \cdot 2Et_2S$ suggested by (Tschugaeff, *Zeit. anorg. Chem.*, 1913, **82**, 420). That

* In this paper the benzyl radical, $C_6H_5.CH_2$ will be written as Bz.

it is not a molecular compound of $PtCl_4 \cdot 2Bz_2S$ and $PtCl_2 \cdot 2Bz_2S$ is further proved by the fact that it could not be broken up on crystallisation from any of the solvents like benzene, chloroform, naphthalene—in which the substance was soluble—and also by the fact that by the action of bases, it has not yet given any compound of the type $PtCl_4 \cdot nB$ (when B=bases) (*vide infra*), which would have been expected had $PtCl_4 \cdot 2Bz_2S$ been one of its components. These properties of the compound may be contrasted with a true molecular compound, $PtCl_3 \cdot 2Et_2S$, whose constitution has been discussed by Rây and Bose-Rây and by Rây, Guha and Bose-Rây (*loc. cit.*). $PtCl_3 \cdot 2Et_2S$ breaks up on crystallisation from alcohol into $PtCl_4 \cdot 2Et_2S$ and $PtCl_2 \cdot 2Et_2S$ and with bases gives compounds both of the type $PtCl_4 \cdot nB$ and $PtCl_2 \cdot nB$ (*loc. cit.*). It appears improbable that the compound $PtCl_3 \cdot 2Bz_2S$ has the constitution $[Pt(Bz_2S)_4] \cdot PtCl_6$ because $PtCl_3 \cdot 2Bz_2S$ seldom gives a compound of the nature, $[Pt\,B_4]\,PtCl_6$ (B=Base), *i.e.*, a compound of the empirical formula $PtCl_3 \cdot 2B$.

Hence, so far as the evidence goes, $PtCl_3 \cdot 2Bz_2S$ appears to be a true compound of trivalent platinum possessing the constitution,

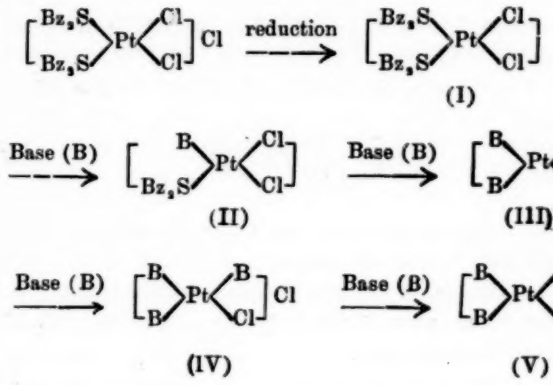
$$\left[\begin{matrix} Bz_2S \\ Bz_2S \end{matrix}\!\!>\!Pt<\!\!\begin{matrix} Cl \\ Cl \end{matrix}\right]Cl.$$

The co-ordination number is 4, and one chlorine atom is outside nucleus. This chlorine atom should behave differently from the other two, and should be ionisable and more labile and hence more reactive than the other two. It could not be proved directly that this chlorine atom outside the nucleus is ionisable as no ionising solvent could be found for the substance, in which its conductivity or molecular weight could be determined. That this chlorine atom is labile and hence reactive has however been amply proved by the action of bases on this compound.

Action of Bases on $PtCl_3 \cdot 2\,Bz_2S$.

The first action of the bases in most cases appears to reduce the compound, so that $PtCl_2 \cdot 2Bz_2S$ is obtained and the base then enters the nucleus by substituting benzyl sulphide molecules, the substitution probably taking place in stages, though owing to inherent difficulty in arresting a reaction in the intermediate stages, partially substituted compounds could seldom be isolated. The base

may then further replace the chlorine atoms within the complex, so that the remaining two chlorine atoms come outside the nucleus and become ionisable. The following scheme illustrates the principle:—



(I) (II) (III) (IV) (V)

The following compounds of the different types indicated above have been obtained:—

Type (I).—$PtCl_2 \cdot 2Bz_2S$ obtained by the action of dimethyl-aniline on $PtCl_2 \cdot 2\,Bz_2S$ (the compound is the same as that obtained from chloroplatinic acid and benzylsulphide direct; *vide supra*).

Type (III).—$PtCl_2 \cdot 2PhNH_2$.

Type (IV).—$PtCl_2 . 3C_5H_{11}N$.

Type (V).—$PtCl_2 \cdot 4\,NH_3$; $PtCl_2 \cdot 4BzNH_2$; $PtCl_2(en)_2$; $PtCl_2 . 4Py$, where en=ethylene diamine; Py=pyridine.

The exceptions are $Pt_2Cl_7 \cdot 4Py$ and $PtCl_2 \cdot Bz_2S \cdot 2\,C_5H_{11}N$.

Most of the above compounds are well known Werner compounds and have also been obtained by Rây, Guha and Bose-Rây and by Rây, Bose-Rây and Adhikari by the action of bases on $PtCl_2 \cdot 2\,Et_2S$, $PtCl_2 \cdot 2\,Et_2S$ and $PtCl_2 \cdot (C_2H_4)_2S_2$ (*loc. cit*) and fully discussed.

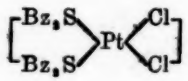
That the compounds $PtCl_2 \cdot 4NH_3$, $PtCl_2 . 4Py$, and $PtCl_2(en)_2$ are true compounds of the Type (V), possessing the constitution $[Pt\,B_4]Cl_2$, (B=NH_3, pyridine and ½ ethylene diamine) has been shown by determining the ionisability of these compounds. All of them have both the chlorine atoms ionisable [*vide* Experimental; also Rây, Bose-Rây and Adhikari (*loc. cit*).]

The compound $Pt_2Cl_7 \cdot 4\,Py$ (see above) would appear to be a molecular compound of $PtCl_4 \cdot 2\,Py$ and $PtCl_2 \cdot 2Py$, but as the substance was insoluble in common solvents it could not be broken up

into its constituents. Rây, Bose-Rây and Adhikari have also obtained this compound from $PtCl_2 \cdot (C_2H_5)_2S_2$ (*loc. cit.*).

The Compound, $PtCl_2 \cdot 2\,Bz_2S$.

This compound previously obtained by Londahl from K_2PtCl_6 and benzyl sulphide (*J. pr. Chem.*, 1888, **38**, 521) is a normal compound of bivalent platinum and possesses the constitution,



The action of bases on it has not yet been studied fully but it should evidently follow the scheme given for $PtCl_2 \cdot 2Bz_2S$ as indicated by (II) to (V). The reaction with pyridine confirms this, as the compounds $PtCl_2 \cdot 2Py$ (Type III) and $PtCl_2 \cdot 4Py$ (Type V) have been obtained.

Experimental.

Chloroplatinic Acid and Benzyl Sulphide.

To an alcoholic solution (rectified spirit) of platinic chloride, benzyl sulphide was added, keeping the platinic chloride slightly in excess and heated under reflux for 4 to 5 hours. It was filtered hot. The filtrate on cooling, gave a crop of fine silky light yellow crystals which were filtered off and the mother-liquor was used over again to extract further quantities of the soluble portion from the insoluble residue. The insoluble portion was then heated under reflux twice with alcohol and filtered off. The silky yellow crystals that came down from the combined filtrates were washed with rectified spirit and then with ether to remove any excess of benzyl sulphide, and dried. The substance was greenish when crystallised from benzene, m. p. 159°. (Found: Pt, 27·96; Cl, 10·5; S, 9·23*. $PtCl_2 \cdot 2Bz_2S$ requires Pt, 28·1; Cl, 10·23; S, 9·22 per cent.).

The portion insoluble in alcohol was then washed with ether and recrystallised from benzene; m.p. 183°. (with decomp.) (Found: Pt, 26·27; Cl, 14·21, 15·14; S, 9·19. $PtCl_2 \cdot 2Bz_2S$ requires Pt, 26·7; Cl, 14·6; S, 8·77 per cent.).

* For estimation of sulphur, Carius' method followed by fusion with Na_2CO_3 and KNO_3 was employed. The nitric acid in the Carius' method was also supplemented by the addition of bromine. The reasons for these are given in *J. Indian Chem. Soc.* 1925, **2**, 185 (footnote).

The Compound $Pt_2Cl_5.4Bz_2S$.

When in the above reaction, platinic chloride was used in large excess, the first crop of the crystals that came down was reddish (instead of light yellow). In that case, the mother-liquor after the separation of the first crop of crystals was again treated with more benzyl sulphide and heated under reflux, when the two usual products $PtCl_2 \cdot 2Bz_2S$ and $PtCl_2 \cdot 2Bz_2S$ were obtained. The reddish crystals obtained as stated above were washed with alcohol and ether and dried; m.p. 158°. (Found: Pt, 27·66; Cl, 12·39. $Pt_2Cl_5 \cdot 4Bz_2S$ requires Pt, 27·4; Cl, 12·47 per cent.).

The substance, $Pt_2Cl_5 \cdot 4\ Bz_2S$ when crystallised from alcohol broke up into $PtCl_2 \cdot 2\ Bz_2S$ and $PtCl_2 \cdot 2\ Bz_2S$. $PtCl_2 \cdot 2\ Bz_2S$ as usual remained insoluble, while $PtCl_2 \cdot 2\ Bz_2S$ crystallised out from the hot filtrate as it cooled down. Both of them were washed and dried as before. The $PtCl_2 \cdot 2\ Bz_2S$ and $PtCl_2 \cdot 2\ Bz_2S$ thus obtained were identified by their melting points, solubility and colour. The percentage of platinum in each case was determined. (Found: Pt, 26·50. $PtCl_2 \cdot 2\ Bz_2S$ requires Pt, 26·7 per cent. Found: Pt, 28·33. $PtCl_2 \cdot 2\ Bz_2S$ requires Pt, 28·1 per cent.).

Molecular Weight Determination of $PtCl_2 \cdot 2Bz_2S$ *in Naphthalene by the Cryoscopic Method.*

No. of observations.	Amount of solvent in grams.	Amount of $PtCl_2 \cdot 2\ Bz_2S$ in grams.	Lowering of freezing point.	M.W. (found).	M.W. (calc.)
I.	34·3	1·0806	0·320°C	679	729
II.	37·5	2·0761	0·555°C	688	729

From the table we see that the molecular weight found by the cryoscopic method in napthalene is about 680, whereas the molecular weight calculated, assuming $PtCl_2 \cdot 2\ Bz_2S$ to be a simple molecule, is 729. The agreement is sufficient to conclude that $PtCl_2 \cdot 2Bz_2S$ consists of single molecules.

Action of Ammonia on $PtCl_2 \cdot 2Bz_2S$.

$PtCl_2 \cdot 2\ Bz_2S$ was covered up with a large excess of liquor ammonia in a flask, corked up and set aside and shaken daily for 3 weeks. It was then filtered and the filtrate evaporated to a very small bulk and diluted with alcohol. The first portions of the

precipitate were redissolved in a small amount of water and reprecipitated with alcohol. (This is necessary to remove any NH_4Cl which might be formed in the reaction). The first portion of the precipitate filtered off, washed with ether and dried, was brownish in colour and did not melt. (Found: Pt, 58·14; Cl, 21·07; N, 16·48. $PtCl_2 \cdot 4\ NH_3$ requires Pt, 58·38; Cl, 21·26; N, 16·76 per cent.).

The Ionisability of $PtCl_2.4NH_3$ *(precipitation method).*

The substance was dissolved in water and precipitated by $AgNO_3$ solution in the cold. No nitric acid was added, lest it should break up the complex. The result obtained is low, but sufficiently convincing to indicate that both the chlorine atoms are ionisable. (Found: Cl, 19·42. $PtCl_2 \cdot 4NH_3$ (assuming both the chlorine atoms to be ionisable) requires Cl, 21·26 per cent.).

Action of Benzylamine on $PtCl_2 \cdot 2Bz_2S$.

$PtCl_2 \cdot 2\ Bz_2S$ was just covered with benzylamine and stirred with a rod. Great heat was evolved and hence during the reaction, which required 15 to 20 minutes, the mass was occasionally cooled by tap water. The mass was extracted with benzene, filtered and the filtrate allowed to evaporate. The residue left after the evaporation of benzene was brownish owing to enclosed tarry matters. It was washed several times with cold alcohol until an almost white substance was left. It was finally washed with hot alcohol and crystallised from chloroform; m. p. 195°. (Found: Pt, 28·42; Cl, 10·32; N, 8·43. $PtCl_2 \cdot 4BzNH_2$ requires Pt, 28·1 ; Cl, 10·23, N, 8·07 per cent.).

Action of Ethylene Diamine on $PtCl_2 \cdot 2\ Bz_2S$.

A 5% solution of ethylene diamine hydrate was added (slightly in excess) to $PtCl_2 \cdot 2\ Bz_2S$ in a hard glass test tube and heated on a water-bath until almost the whole went into solution (2 to 3 hours). It was allowed to cool, when benzyl sulphide separated out. This was filtered off and the filtrate evaporated to a small volume in a vacuum desiccator and precipitated with alcohol. The first crop of the precipitate was redissolved in a small amount of water and reprecipitated with alcohol. This is necessary to free the substance from the hydrochloride of the base that might be formed in the reaction. The substance was brownish, hygroscopic and did not melt up to 230°. (Found: Pt, 49·91; Cl, 17·56; N, 14·16. $PtCl_2 \cdot C_2H_4(NH_2)_2$ requires Pt, 50·51; Cl, 18·39; N, 14·50 per cent.).

The Ionisability of $PtCl_2\ en_2$ *(precipitation method).*

The substance was dissolved in water and $AgNO_3$ solution added in the cold without adding nitric acid. The result obtained is slightly low. (Found: Cl, 17·60. $PtCl_2(en)_2$ (assuming both Cl atoms ionisable) requires Cl, 18·39 per cent.).

Action of Pyridine on $PtCl_2 \cdot 2\ Bz_2S$.

$PtCl_2 \cdot 2\ Bz_2S$ was digested with an excess of pyridine on a water-bath for 6 to 8 hours, filtered hot and extracted 2 or 3 times with hot pyridine. The pyridine extracts were allowed to cool, when a white crystalline substance came down, which was filtered off and washed with ether several times. The substance was extremely soluble in water and was very hygroscopic. It turned yellow at 140° but did not melt. (Found: Pt, 33·09; Cl, 12·02; N, 8·7. $PtCl_2 \cdot 4\ C_5H_5N$ requires Pt, 33·5; Cl, 12·19; N, 9·6 per cent.)

The insoluble portion was washed a few times more with hot pyridine, then with alcohol and water to remove the last traces of the white compound which was very soluble in water. It was then washed with alcohol, benzene and ether. The substance was insoluble in common organic solvents and did not melt. (Found: Pt, 40·48; Cl, 26·75; N, 5·48; C, 24·85; H, 2·18. $Pt_2Cl_4 \cdot 4\ C_5H_5N$ requires Pt, 40·8; Cl, 26·03; N, 5·86; C, 25·09; H, 2·09 per cent.).

The Ionisability of $PtCl_2 \cdot 4Py$.

(Found: Molecular conductivity at 1221 litres dilution (which may be practically taken to be infinite dilution)=276.

Hence, the substance is a ternary electrolyte (theoretical value for which is 260), that is, both the Cl atoms are ionisable.

Action of Aniline on $PtCl_2 \cdot 2\ Bz_2S$.

$PtCl_2 \cdot 2Bz_2S$ was digested with an excess of aniline on a water-bath for 3 to 4 hours. A reddish violet solution was obtained. This was filtered and the residue washed thoroughly with alcohol, until the filtrate was no longer coloured violet. It was then washed twice with water and again with alcohol and finally with ether and dried. The substance was dirty grey in colour and did not melt. (Found: Pt, 43·47; Cl, 16·01; N, 6·85. $PtCl_2 \cdot 2\ PhNH_2$ requires Pt, 43·14; Cl, 15·70; N, 6·2 per cent.).

The coloured filtrate contained mainly the oxidation products of aniline with only traces of platinum.

Action of Dimethylaniline on $PtCl_4 \cdot 2Bz_2S$.

$PtCl_4 \cdot 2Bz_2S$ was treated with a slight excess of dimethylaniline in a hard glass test tube and heated on a water-bath for 2 to 3 hours with occasional stirring with a rod. A deep violet solution was obtained. Alcohol was added and the solution filtered. The insoluble portion was washed several times with alcohol until the filtrate was no longer violet. The residue was then crystallised from hot benzene, washed with alcohol and ether and dried. The substance was obtained as greenish crystals, m.p. 159°. (Found: Pt, 28·13; Cl, 9·93; S, 8·97. $PtCl_4 \cdot 2Bz_2S$ requires Pt, 28·1; Cl, 10·23; S, 9·22 per cent.).

The substance $PtCl_4 \cdot 2Bz_2S$ is the same as that obtained direct from chloroplatinic acid and benzylsulphide (*vide supra*).

The filtrate contained mainly oxidation products of dimethylaniline and was rejected.

Action of Piperidine on $PtCl_4 \cdot 2Bz_2S$.

(*i*) About 2 c.c. of piperidine were added to about 1 g. of $PtCl_4 \cdot 2Bz_2S$ in a hard glass test tube and stirred with a rod. Great heat was evolved and the mass was occasionally cooled by tap water. The reaction was allowed to proceed for about 25 minutes. The semi-solid mass obtained was completely soluble in chloroform. The chloroform solution was allowed to evaporate to a small bulk and precipitated with ether. It was filtered and the precipitate freed from chloroform, washed with water, dried in a desiccator and dissolved in the smallest quantity of chloroform and reprecipitated with ether. The precipitate was filtered and dried. The substance was white with slight brownish tinge, m.p. 172°. (Found: Pt, 28·34; Cl, 14·91; N, 5·00. $PtCl_4 \cdot 2C_5H_{11}N \cdot Bz_2S$ requires Pt, 28·42; Cl, 15·52; N, 4·08 per cent.).

(*ii*) Piperidine was added in excess to $PtCl_4 \cdot 2Bz_2S$ in a hard glass test tube and stirred with a rod. Great heat was evolved as before. The reaction was allowed to take place for more than half an hour. The mass was dissolved in chloroform and precipitated with ether. The process was repeated as before, and the precipitate washed with water and ether and dried. The substance was white with a brownish tinge. (Found: Pt, 37·19; Cl, 13·97;

N, 8·16. $PtCl_2 \cdot 3C_5H_{11}N$ requires Pt, 37·4 ; Cl, 13·62; N, 8·06 per cent.).

Action of Pyridine on $PtCl_2 \cdot 2\ Bz_2S$.

$PtCl_2 \cdot 2\ Bz_2S$ was digested with in excess of pyridine in a hard glass test tube on a water-bath for 5 to 6 hours, and filtered hot. The residue was extracted once or twice with hot pyridine. The combined pyridine extracts and the filtrate on evaporation gave white crystals, which were filtered off, washed with cold pyridine once and then thoroughly with chloroform, benzene and ether. The substance was white, had no m.p. but turned yellow above 140°. (Found: Pt, 33·07; Cl, 11·56. $PtCl_2 \cdot 4\ C_5H_5N$ requires Pt, 33·50; Cl, 12·19 per cent.).

The substance is identical with that obtained from $PtCl_2 \cdot 2Bz_2S$ and pyridine (*vide supra*).

The pyridine-insoluble portion was digested repeatedly with boiling chloroform and filtered hot until almost the whole went into solution. The filtrate, on spontaneous evaporation, gave fine yellow crystals, insoluble in water. These were collected, washed with chloroform (cold), ether, alcohol, water and again with alcohol and ether. (Found: Pt, 46·3; Cl, 17·01; N, 6·50. $PtCl_2 \cdot 2\ C_5H_5N$ requires Pt, 46·0 ; Cl, 16·75 ; N, 6·60 per cent.).

$PtCl_2 \cdot 4Py$ on being heated above 140° gave the yellow substance $PtCl_2 \cdot 2Py$ which was extracted with boiling chloroform as above, dried and analysed. (Found: Pt, 46·2. $PtCl_2 \cdot 2C_5H_5N$ requires Pt, 46·0 per cent.).

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Hetero-ring Formations with Thiocarbohydrazide. Part III. Reactions of Substituted Thiocarbohydrazides.

By Praphulla Chandra Guha and Satyendra Kumar Roy-Choudhury.

Two different methods of preparation of thiocarbohydrazide are known of which one is due to Curtius and Heidenreich (*J. pr. Chem.*, 1895, ii, **52**, 586) and the other is due to Guha and De (*J. Chem. Soc.*, 1924, **125**, 1215). Though thiocarbohydrazide and a few of its typical reactions and a number of heterocyclic compounds derived from it have been studied (Guha and De, *J. Indian Chem. Soc.*, 1924, **1**, 141 ; 1926, **2**, 225) no alkyl or aryl substituted derivative of this compound is known. Two extremely reactive hydrazino groups are present in thiocarbohydrazide, of which one can be made inert by substitution. So, it was expected that though substituted and unsubstituted thiocarbohydrazides form members of the same family they will react differently towards different ring-closing agents. With this object in view, which has been fully realised, aryl-substituted thiocarbohydrazides have been prepared by a new method and their behaviour towards various types of organic substances has been investigated. 1-Phenyl-, 1-tolyl- and 1 : 1′-phenyl-methyl-thiocarbohydrazides * have been prepared by the action of hydrazine hydrate upon phenyl-, *m*-tolyl- and methyl-phenyl-dithiocarbazinate thus :—

$$RR'N{\cdot}NH{\cdot}CSSCH_3 + NH_2{\cdot}NH_2 = RR'N{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH_2 + CH_3SH \qquad \text{(I-VI)}$$

(R = Phenyl or tolyl ; R′ = H or methyl).

* The reaction proceeds mainly in the direction as indicated, but along with the phenyl-substituted thiocarbohydrazide there is always obtained a trace of a substance (m.p. 176-177° ; N, 28·44 ; S, 18·44 per cent.) soluble in alkali but insoluble in water and alcohol which could not be studied further for want of a sufficient quantity of this substance.

The action of aldehydes and ketones proceeds in the normal way to yield the corresponding thiocarbohydrazones (VII-XII).

$PhNH{\cdot}NH.CS.NH{\cdot}N:CHPh$	...	...	(VII)
$PhNH.NH.CS.NH.N:CH.C_6H_4OH$	...	...	(X)
$PhNH.NH.CS.NH.N:CH.C_6H_4NO_2$	...	...	(VIII)
$Me.C_6H_4NH.NH.CS.NH.N:CHC_6H_4NO_2$		...	(XI)
$PhNH.NH.CS.NH.N:CH.CH:CHPh$	...	...	(IX)
$PhNH.NH.CS.NH.N:CH(Me)_2$	...	...	(XII)

The ring-closure of the aldehyde-thiocarbohydrazones has been effected by the oxidising action of ferric chloride; the resulting thiobiazole derivatives may be represented either by formula (*a*) or by (*b*) depending upon the question as to from what part of the molecule a hydrogen atom should tautomerise to convert the thioketonic sulphur into a thiol group.

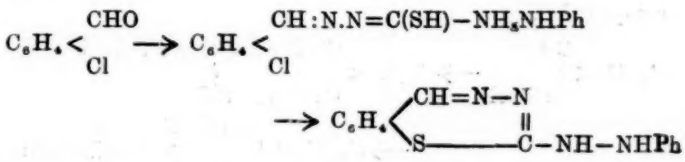
$$PhNH.NH.C(SH)=N-N:CHR \xrightarrow{-H_2} PhNH.NH-\underset{\displaystyle S}{\overset{\displaystyle N-N}{\overset{\|}{C}\quad\overset{\|}{C}}}-R \qquad (a)$$

$$PhNH-N=C(SH)-NH-N:CHR \xrightarrow{-H_2} PhNH{\cdot}N=\underset{\displaystyle S}{\overset{\displaystyle NH-N}{\overset{|}{C}\quad\overset{\|}{C}}}-R \qquad (b)$$

As the oxidation products could not be hydrolysed by boiling with concentrated hydrochloric acid, and no phenylhydrazine could be traced in the solution thus treated, the formula (*b*) where the phenylhydrazino group is attached to the thiobiazole ring by a double linking has been rejected. Thus 2-phenyl-5-phenylhydrazino-1:3:4-thiodiazole (XIII), 2-cinnamyl-5-phenylhydrazino-1:3:4-thiodiazole (XIV) and 2-*p*-nitrophenylhydrazino-1:3:4-thiodiazole (XV) have been obtained from (VII), (IX) and (VIII) respectively.

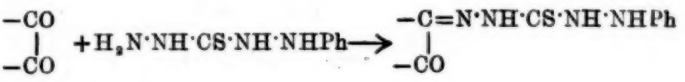
The action of *o*-chlorobenzaldehyde does not only yield a thiocarbohydrazone but it goes a step further and the thiocarbohydrazone first formed gives 2-phenylhydrazino-6:7-benzo-1:3:4-thio-

heptadiazine (XVI) with the loss of a molecule of hydrochloric acid, thus:

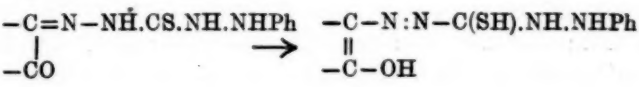


That the sulphur atom is present as a member of the ring is proved by the fact that the compound cannot be desulphurised by treatment with mercuric oxide.

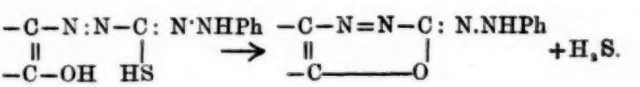
Phenylthiocarbohydrazide reacts with phenanthraquinone and acenaphthaquinone to yield phenylhydrazones of 2:3-phenanthro-6-keto-1:4:5-oxdiazine (XVII) and 2:3-acenaphtho-6-keto-1:4:5-oxdiazine (XVIII). The first stage of the reaction consists in the formation of thiocarbohydrazone, thus:



which then assumes the azo-structure by the migration of one hydrogen atom, thus:



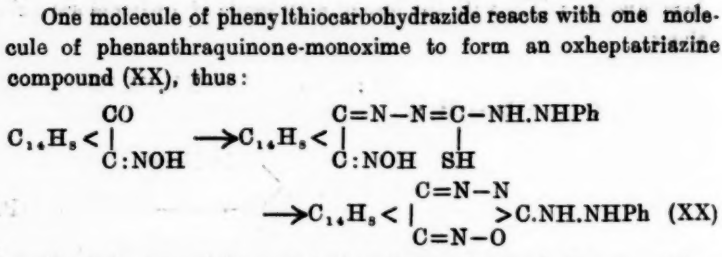
The azo-compound then loses a molecule of hydrogen sulphide to give rise to an oxdiazine compound, thus:



m-Tolylthiocarbohydrazide similarly gives a compound (XIX) with phenanthraquinone.

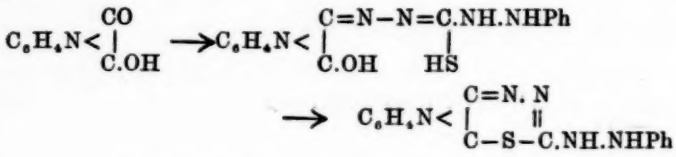
It will be seen that this reaction is quite different from those observed by Guha and De in the case of thiocarbohydrazide and *o*-diketones like benzil, acenaphthaquinone, camphorquinone, alloxan, phenanthraquinone and isatin when 3-thioketo-1:2:4:5-hepta-tetrazines and di-phenanthra-(and di-isatino)-thiocarbohydrazone were respectively formed (*J. Indian. Chem. Soc.*, 1925, **2**, 225).

One molecule of phenylthiocarbohydrazide reacts with one molecule of phenanthraquinone-monoxime to form an oxheptatriazine compound (XX), thus:



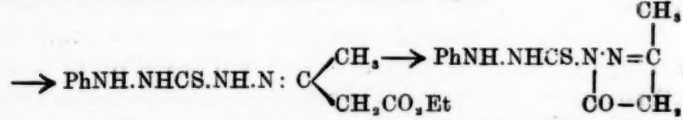
The behaviour of thiocarbohydrazide itself towards the monoxime has, however, been found to take place in a quite different manner by Guha and De (*loc. cit.*) when a thioketo-bis-triazine compound is formed.

Isatin reacts with phenylthiocarbohydrazide to yield a thiodiazine, thus:



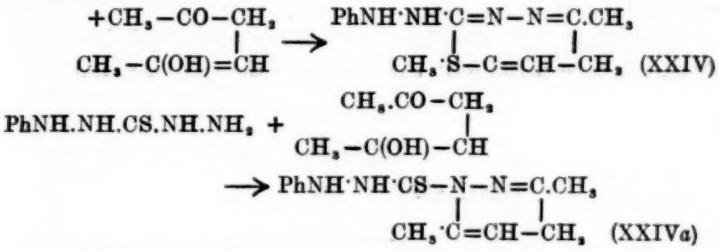
Action of β-Ketonic Esters and 1:4-Diketones.

The hydrazones and oximes of β-ketonic esters easily give up alcohol and are converted into pyrazolones (*cf.* *J. pr. Chem.*, **39**, 153; **52**, 23, 45; **51**, 43, 140, 157; *Ber.*, **28**, 2731; *Annalen*, **922**, 5; *Ber.*, **19**, 219). De (*J. Indian Chem. Soc.*, 1926, **3**, 30) has prepared carbamido- and carbothioamido-pyrazolones by treating semi- and thiosemi-carbazones of acetoacetic ester by the action of alcoholic ammonia. In the present instance, phenylthiocarbohydrazide has been found to react with acetoacetic ester to yield first of all a phenylthiocarbohydrazone (XXII) which loses a molecule of alcohol on treatment with sodium ethoxide to yield 1-carbothiophenylhydrazido-3-methyl-5-pyrazolone (XXIII) thus:—



With acetonylacetone it reacts readily to yield 2-phenylhydrazino-5:8-dimethyl-1:3:4-thio-octadiazine (XXIV). The possible heptadiazine formula (XXIV*a*) has been rejected on the ground that the

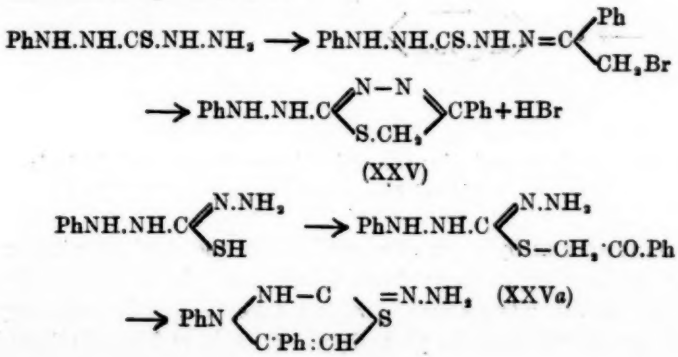
compound actually isolated is insoluble in alkali and cannot be desulphurised by mercuric oxide.



Blaise (*Compt. rend.*, 1921, **172**, 221) has shown that acetonylacetone reacts with semicarbazide to yield a disemicarbazone in the first stage which gives N-carbamido-2: 5-dimethylazole by the loss of one molecule of semicarbazide. A comparison of the above two reactions would suggest that the thiol-hydrogen atom of phenylthiocarbohydrazide is more easily attacked by a hydroxyl than by an ethoxyl group.

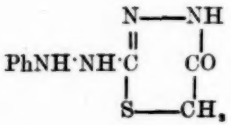
Action of Halogenated Ketones and Esters.

Condensation of thiosemicarbazides with ω-bromacetophenone leads simultaneously to the formation of thiodiazine and thiodiazole derivatives (Bose, *J. Indian Chem. Soc.*, 1924, **1**, 53; 1925, **2**, 95) with preponderance of the first compound. The behaviour of the ω-bromoketone towards 1-phenylthiocarbohydrazide is analogous to Bose's reaction with this difference, however, that the reaction proceeds in this case only in one direction with the exclusion of the thiodiazole compound, thus:—

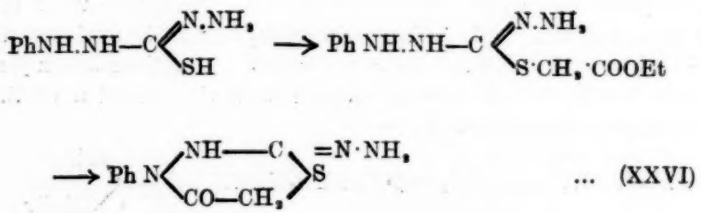


The alternative formula (XXV*a*) has been rejected on the ground that a compound containing the group (:N.NH$_2$) would have formed compounds with aldehydes very readily, whereas the compound actually isolated does not do so.

By analogy with the above reaction it was expected that monochloracetic ester would form a compound of the following formula,



but the compound isolated possesses a hydrazino group as is proved by the fact that it readily forms a benzylidene derivative with benzaldehyde. This difference in behaviour of ω-bromacetophenone and monochloracetic ester can only be accounted for by assuming that the ketonic group of the former reacts with the hydrazino side of the hydrazide to form brom-acetophenone-phenyl thiocarbohydrazone which then loses a molecule of hydrobromic acid to form the thiodiazine ring; whereas, with monochloracetic ester one molecule of HCl is eilminated first forming a carbethoxy-methyl-thioether which in its turn loses a molecule of alcohol, thus:—



... (XXVI)

Action of ω-Bromacetophenone and Chloracetic ester on Aldehyde-phenylthiocarbohydrazones.

As there is no hydrogen atom available in the farthest nitrogen atom of the aldehyde-phenylthiocarbohydrazone, the (OH) and (OEt) groups of the intermediate products take away the necessary hydrogen atoms from the phenylhydrazino side and are eliminated

in the shape of water and alcohol respectively, to yield thiodiazine derivatives (XXVII), (XXIX) and (XXX) thus:—

$$HO.C_6H_4.CH=N.N=C(SH)\cdot NH.NHPh + ClCH_2COOEt$$

$$\longrightarrow HO.C_6H_4.CH:N.N:C\begin{cases}NH.NPh\\ S-CH_2\end{cases}CO \qquad \text{(XXVII)}$$

$$C_6H_5CH=N.N=C(SH).NH.NHPh$$

$$\longrightarrow C_6H_5CH=N.N=C\begin{cases}NH.NPh\\ S-CH_2\end{cases}CO \qquad \text{(XXIX)}$$

$$HO.C_6H_4.CH=N.N:C(SH)-NH-NHPh + BrCH_2COPh$$

$$=HO.C_6H_4.CH:N.N=C\begin{cases}NH.NPh\\ S-CH\end{cases}CPh$$

(XXX)

Compounds (XXVII) and (XXIX) on hydrolysis give compounds which react very readily with aldehydes and mustard oils proving the presence of reactive hydrazino groups in the hydrolysed products.

$$HO.C_6H_4\cdot CH:N.N:C\begin{cases}NH.NPh\\ S-CH_2\end{cases}CO$$

$$\xrightarrow{\text{hydrolysis}} H_2N.N:C\begin{cases}NH\cdot NPh\\ S-CH_2\end{cases}CO \qquad \text{(XXVIII)}$$

Experimental.

Phenylthiocarbohydrazide (I).—Hydrazine hydrate (2·5 g.) was added to methylphenyldithiocarbazinate (10 g.) in alcoholic suspension and the mixture shaken when the reaction began at once with evolution of heat. The mixture was then heated under reflux for about two hours, filtered after staying overnight and the separated crystalline mass was washed with benzene to dissolve

away the adhering tarry matters and crystallised successively from boiling water and alcohol in white rectangular plates, m.p. 149-150° (yield 2·5 gms.).

It is soluble in alcohol, acetic acid, pyridine and caustic alkalis sparingly soluble in chloroform, acetone, benzene, toluene and hydrochloric acid. (Found: N, 30·62; S, 17·02. $C_7H_{10}N_4S$ requires N, 30·77; S, 17·58 per cent.).

About 0·2 g. of a substance insoluble in water and alcohol was obtained from the reaction mixture.

The Hydrochloride (II).—1-Phenylthiocarbohydrazide was dissolved in boiling water and stirred with an excess of hydrochloric acid; on cooling, white crystalline plates separated out, m.p. 181°. It becomes light brown on exposure to the air. (Found: N, 25·91. $C_7H_{10}N_4S$, HCl requires N, 25·68 per cent.).

Ethyl m-*Tolyldithiocarbazinate* (III) was prepared by adding carbonbisulphide (20 g.) and potassium hydroxide (11 g.) dissolved in water under cooling to a solution of *m*-tolylhydrazine (24 g.) dissolved in 75 c.c. of alcohol. Ethyl bromide (11 g.) was then added to it under cooling; the solution after standing for some time separated crystals which were filtered, washed with alcohol and crystallised from the same solvent in white plates, m.p. 99°. It dissolves in alkali and is precipitated by acids (yield 2 gm.). (Found: N, 12·02. $C_{10}H_{14}N_2S_2$ requires N, 12·39 per cent.).

m-*Tolylthiocarbohydrazide* (IV).—A mixture of absolute alcohol (10 c.c.), the above carbazinate (10 g.) and hydrazine hydrate (10 g.) was heated under reflux for two hours. On cooling, crystals were deposited which were further purified by crystallisation from alcohol in brownish white plates, m.p. 163-164° with decomp. It is soluble in alkali and is precipitated by dilute acids. (Found: S, 16·02. $C_8H_{12}N_4S$ requires S, 16·32 per cent.).

Ethyl 1:1-*Phenyl-methyl-dithiocarbazinate* (V).—This compound was prepared similarly as compound (III). The separated oil possessing the characteristic odour of a thio-ether was shaked with water, extracted with ether, dried with fused calcium chloride, the ether distilled off and the oil was finally distilled under reduced pressure. (Found: N, 12·71. $C_{10}H_{14}N_2S_2$ requires N, 12·44 per cent.).

1:1-*Methyl-phenyl-thiocarbohydrazide* (VI).—The above ester (15 g.) was heated under reflux with 20 c.c. of absolute alcohol and 5 g. of hydrazine hydrate for 2 hours on the water-bath. The insoluble crystalline mass thus obtained was crystallised from a large quantity

of alcohol in white plates, m.p. 228-229° with decomp. (Found: N, 28·78. $C_8H_{12}N_4S$ requires N, 28·57 per cent.).

Benzaldehyde-1-phenylthiocarbohydrazone (VII).—Benzaldehyde (1·1 g.) and 4-phenylthiocarbohydrazide (1·8 g.) in alcoholic solution heated under reflux for a few minutes when a white insoluble product separated from the solution and was crystallised from acetic acid in white plates, m.p. 185° (yield quantitative). (Found: N, 20·62. $C_{14}H_{14}N_4S$ requires N, 20·74 per cent.).

p-*Nitrobenzaldehyde-1-phenylthiocarbohydrazone* (VIII).—The compound was crystallised from acetic acid in white rectangular plates, m.p. 192° with a red colouration. (Found: N, 22·1. $C_{14}H_{13}O_2N_5S$ requires N, 22·22 per cent.).

Cinnamicaldehyde-1-phenylthiocarbohydrazone (IX).—It was crystallised from acetic acid in light yellow plates, m. p. 167-198° (yield is almost quantitative). (Found: S, 10·42. $C_{16}H_{16}N_4S$ requires S, 10·82 per cent.).

Salicylaldehyde-1-phenylthiocarbohydrazone (X).—The compound was crystallised from a large quantity of alcohol in white needles, m.p. 206° with decomposition (yield is almost quantitative). (Found: N, 19·29. $C_{14}H_{14}ON_4S$ requires N, 19·59 per cent.).

p-*Nitrobenzaldehyde-1-m-tolylthiocarbohydrazone* (XI).—It was crystallised from acetic acid in light yellow rectangular plates, m.p. 165 166°. (Found: N, 21·48. $C_{15}H_{15}O_2N_5S$ requires N, 21·27 per cent.).

Acetone-1-phenylthiocarbohydrazone (XII).—A mixture of acetone and 1-phenylthiocarbohydrazide was heated under reflux for 1½ hours. On concentration and cooling a crystalline product began to separate out. After standing for about an hour it was filtered and crystallised from the same solvent in white plates, m.p. 162°. (Found: N, 25·21. $C_{10}H_{14}N_4S$ requires N, 25·22 per cent.).

2-*Phenyl-5-phenylhydrazino-1:3:4-thiodiazole* (XIII).—An aqueous solution of thoroughly powdered benzaldehyde-1-phenylthiocarbohydrazone (2 g.) was heated under reflux with an excess of ferric chloride solution for 15 to 20 minutes. The orange-coloured crystalline product thus obtained was filtered, washed with water, boiled with animal charcoal in alcoholic solution for half an hour and filtered hot; orange coloured needle-shaped crystals were obtained from the solution on cooling, m.p. 172°. It is insoluble in acid and alkali. (Found: N, 20·65. $C_{14}H_{12}N_4S$ requires N, 20·82 per cent.).

2-*Cinnamyl-5-phenylhydrazino-1:3:4-thiodiazole* (XIV).—This compound was prepared exactly in a similar way as the preceding

compound from cinnamic aldehyde-1-phenylthiocarbohydrazone and was crystallised from alcohol in dark red plates. It shrinks at 168° and melts at 173° (yield is quantitative). It is insoluble in acid and alkali. (Found: S, 10·51. $C_{16}H_{14}N_4S$ requires S, 10·88 per cent.).

2-p-*Nitrophenyl-5-phenylhydrazino*-1:3:4-*thiodiazole* (XV).—The method of procedure was the same as in the case of the preceding compound. It was crystallised from acetic acid in golden-yellow plates, m.p. 263-264°. (Found: N, 22·52. $C_{14}H_{11}O_2N_5S$ requires N, 22·37 per cent.).

2-*Phenylhydrazino*-6:7-*benzo*-1:3:4-*thioheptadiazine* (XVI).—1-Phenylthiocarbohydrazide(0·9 g.) and *o*-chlorbenzaldehyde (0·7 g.) in alcoholic solution were heated under reflux for ten minutes when a crystalline product separated out. It was filtered hot, washed with alcohol and crystallised from acetic acid in pale yellow plates, m.p. 195°. The compound was proved to be free from chlorine and could not be desulphurised by mercuric oxide treatment. (Found: N, 20·78. C $H_{12}N_4S$ requires N, 20·89 per cent.).

Action of Diketones and their Monoximes.

Phenylhydrazone of 2:3-*Phenanthra*-6-*keto*-1:4:5-*oxdiazine* (XVII).—A mixture of phenanthraquinone (4 g.) and 1-phenylthiocarbohydrazide (3·5 g.) in acetic acid solution was heated under reflux. The reaction began at once, the solution became dark in colour and hydrogen sulphide began to evolve. After heating for about an hour, the separated red crystalline product was washed with acetic acid and was crystallised from nitrobenzene in reddish green rectangular plates, m.p. above 300°. (yield 1 gm.). It is insoluble in acids and alkalis and produces a deep blue colouration with concentrated sulphuric acid. (Found: N, 16·32. $C_{21}H_{14}ON_4$ requires N, 16·57 per cent.). The compound was proved to be free from sulphur.

m-*Tolylhydrazone of* 2:3-*Phenanthra*-6-*keto*-1:4:5-*oxdiazine* (XIX).—An acetic acid solution of phenanthraquinone (3·5 g.) and *m*-tolylthiocarbohydrazide (2 g.) was heated under reflux for 1½ hours. The insoluble precipitate thus obtained crystallised from nitrobenzene in reddish green plates, m.p. above 295° (yield 0·8 gm.). It is insoluble in acid and alkali. (Found: N, 16·30. $C_{22}H_{16}ON_4$ requires N, 15·92 per cent). The absence of sulphur in this compound was also proved.

Phenylhydrazone of 2:3-*Acenaphtha*-6-*keto*-1:4:5-*oxdiazine* (XVIII).—Acenaphthaquinone (3 g.) and 1-phenylthiocarbohydrazide (3 g.) in acetic acid solution were heated under reflux for 4-5 hours. The solution on concentration and cooling yielded a solid product which was crystallised from pyridine in shining black needles, m.p. above 300°. It is insoluble in acid and alkali (yield 1 g.). (Found: N, 18·23. $C_{18}H_{12}ON$ requires N, 17·95 per cent.).

Phenylhydrazone of 3:4-*Phenanthra*-7-*keto*-1:2 5:6-*heptaoxtriazine* (XX).—Phenanthraquinone monoxime (2·5 g.) and 1-phenylthiocarbohydrazide (1·9 g.) in acetic acid solution were heated under reflux for ten minutes. The reaction proceeded vigorously with effervescence due to the rapid escape of hydrogen sulphide. The separated precipitate was filtered from the deep red solution while hot and crystallised from nitrobenzene in reddish green plates, m.p. above 300° (yield 0·7 g.). It is insoluble in acid and alkali. (Found: N, 19·76. $C_{21}H_{15}ON_5$ requires N, 19·82 per cent.).

Phenylhydrazone of 2:3-*Isatino*-6-*keto*-1:4:5-*thiodiazine* (XXI).—A mixture of isatin (2·8 g.) and 1-phenylthiocarbohydrazide (3·6 g.) was heated in acetic acid solution under reflux for two to three hours when a red crystalline precipitate separated out, and was crystallised from a large quantity of acetic acid. It becomes brownish in colour at about 260° and does not melt even at 300° at which temperature it becomes perfectly brown (yield 1·5 gm.) (Found: N, 23·62; S, 10·69. $C_{15}H_{11}N_5S$ requires N, 23·89; S, 10·91 per cent.). It is insoluble in alkali.

Action of 1:3-Ketonic Esters and 1:3-Diketones.

Phenylthiocarbohydrazone of Acetoacetic ester (XXII).—A mixture of 1-phenylthiocarbohydrazide (1·8 g.) and acetoacetic ester (1·3 g.) was heated under reflux in alcoholic solution for one hour. A crystalline product separated out on cooling which was crystallised from alcohol in white plates, m.p. 115-116° (yield 1 gm.). It dissolves in alkali and is precipitated by acids. (Found: N, 19·48. $C_{13}H_{18}O_2N_4S$ requires N, 19·04 per cent.).

1-*Carbothiophenylhydrazido*-3-*methyl*-5-*pyrazolone* (XXIII).—Acetoacetic ester (1·3 g.) was added to 1-phenylthiocarbohydrazide (1·8 g.) dissolved in absolute alcohol (25 c.c. containing 0·3 g. of metallic sodium) and the mixture was heated under reflux for 15 minutes. The light-yellow solid thus obtained was dissolved in

sodium hydroxide solution and precipitated by an excess of hydrochloric acid. It was crystallised from benzene in white plates, m.p. 142° with decomp. (yield 0·8 gm.). (Found: N, 22·73. $C_{13}H_{11}ON_4S$ requires N, 22·59 per cent.). The above compound was also obtained by heating phenylthiocarbohydrazone of acetoacetic ester with alcoholic sodium ethoxide solution.

2-Phenylhydrazino-5:8-dimethyl-1:3:4-octathiodiazine (XXIV).—A mixture of actonylacetone (1·8 g.) and 1-phenylthiocarbohydrazone (2 g.) was heated under reflux in acetic acid solution for 15 minutes when an insoluble product separated out and was crystallised from a large quantity of acetic acid in white plates, m.p. 230° with decomp. It is insoluble in acid and alkali. (Found: N, 21·80. $C_{12}H_{16}N_4S$ requires N, 21·52 per cent.).

2-Phenylhydrazino-5-phenyl-1:3:4-thiodiazole (XXV).—A mixture of 1-phenylthiocarbohydrazide (0·9 g.) and *w*-bromacetophenone (0·5 g.) was covered with a sufficient quantity of acetic acid and briskly shaken. Much heat was evolved and soon a clear solution was obtained from which after about two hours a white insoluble product separated out. It was crystallised from a large quantity of alcohol in white plates, m.p. 199° (yield 0·8 gm.). It is insoluble in acid and alkali. (Found: N, 19·70. $C_{15}H_{14}N_4S$ requires N, 19·86 per cent.).

Hydrazone of 2:5-Diketo-4-phenyl-tetrahydro-1:3:4-thiodiazine (XXVI).—An alcoholic solution of monochloracetic ester (3·6 g.) was added to an alcoholic solution (containing 0·3 g. of sodium) of 1-phenylthiocarbohydrazide (5·4 g.) and the mixture was heated under reflux for three hours. Sodium chloride was removed by filtration while hot and the filtrate yielded a brownish solid on concentration and cooling which was crystallised from dilute alcohol in light brown plates, m.p. 152-153° (yield 1 gm.). It dissolves readily in hydrochloric acid. (Found: N, 25·42. $C_9H_{10}ON_4S$ requires N, 25·23 per cent.).

The *benzal derivative* of (XXVI) was crystallised from alcohol in yellow needles, m.p. 158°. (Found: N, 18·31. $C_{16}H_{14}ON_4S$ requires N, 18·06 per cent.).

Action of Halogenated Ketones and Esters on Aldehyde-phenylthiocarbohydrazones.

2-Salicylaldehydehydrazone of 2:5-Diketo-4-phenyl-tetrahydro-1:3:4-thiodiazine (XXVII).—Monochloracetic ester (1·2 g.) was

added to salicylaldehyde-1-phenylthiocarbohydrazone (2·8 g.) suspended in alcohol and the mixture heated under reflux for about 45 minutes. The clear solution obtained after half an hour's heating, yielded, on heating for a few minutes more, an insoluble product which was crystallised from a mixture of alcohol and pyridine in white long plates, m.p. 220° (yield quantitative). It is insoluble in acid and alkali. (Found: N, 17·36. $C_{16}H_{14}O_2N_4S$ requires N, 17·18 per cent.).

Hydrolysis of the above Compound: Formation of the Hydrazone of 2:5-*Diketo*-4-*phenyl-tetrahydro*-1:3:4-*thiodiazine* (XXVIII).—When boiled with moderately strong hydrochloric acid for one hour, the above thiodiazine compound went into solution. It was filtered hot, the solution on concentration and cooling yielded a crystalline precipitate which was crystallised from a small quantity of water, m.p. 247-248° (with decomp.). (Found: Cl, 13·87. $C_9H_9ON_4S$, HCl requires Cl, 13·73 per cent.).

Benzalhydrazone of 2:5-*Diketo*-4-*phenyl-tetrahydro*-1:3:4-*thiodiazine* (XXIX).—This compound was similarly obtained as compound (XXVII) from benzaldehyde-1-phenylthiocarbohydrazone and was crystallised from alcohol in white plates, m.p. 189° with decomposition. It is insoluble in hydrochloric acid and dissolves with difficulty in alkali. (Found: N, 18·38. $C_{16}H_{14}ON_4S$ requires N, 18·06 per cent.).

Salicylaldehydehydrazone of 2-*Keto*-4:5-*diphenyl*-*dihydro*-1:3:4-*thiodiazine* (XXX).—A mixture of salicylaldehyde-1-phenylthiocarbohydrazone (2·8 g.) and *w*-bromacetophenone (2 g.) was heated in an alcoholic solution under reflux for fifteen minutes when a crystalline solid separated out which was crystallised from acetic acid in chocolate coloured needles, m.p. 221° (yield 2 gm.). It is insoluble in acid and alkali. (Found: N, 14·82. $C_{22}H_{18}ON_4S$ requires N, 14·51 per cent.).

Our thanks are due to Sir P. C. Rây and Prof. J. C. Ghosh for the kind interest they have taken in this work.

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Hetero-Ring Formations with Thiocarbohydrazide. Part IV. Reactions of 1-Phenylthiocarbohydrazide.

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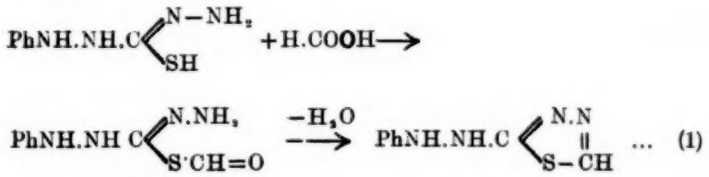
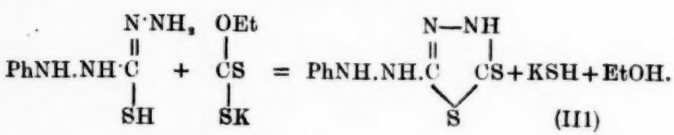
In Part III the preparation of 1-phenylthiocarbohydrazide and its behaviour towards aldehydes and ketones, *o*-diketones and their monoximes, halogenated ketones and esters, β-ketonic esters and 1:4-diketones have been described (see preceding paper). In the present part, the action of acids, acid chlorides, acid anhydrides, mustard oils and *iso*cyanates upon 1-phenylthio-carbohydrazide as also the action of chlorides of dibasic acids upon aldehyde-1-phenylthiocarbohydrazonesand different ring-closing agents upon mustard oil and *iso*cyanate derivatives of the thiocarbo-hydrazide are to be described.

Formic acid reacts with 1-phenylthiocarbohydrazide to yield 2-phenylhydrazino-1:3:4-thiodiazole, thus:



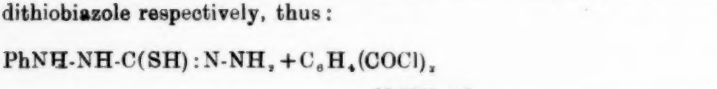
The presence of the sulphur atom in the ring is proved by its stability towards mercuric oxide treatment: moreover, the insolubility of this substance in alkali proves the absence of any thiol group in this compound. With acetic anhydride, the thio compound does not yield any closed-ring compound as in the case of the reaction with formic acid but, simply the mono-acetyl derivative (II) is formed.

Potassium ethyl-xanthate yields 2-phenylhydrazino-5-thiol-1:3:4-thiodiazole and this reaction is quite similar to the reactions studied by Guha (*J. Amer. Chem. Soc.*, 1922, **44**, 1510) with thiosemicarbazides and by Guha and De (*J. Chem. Soc.*, 1924, **125**, 1215) with carbo- and thiocarbo-hydrazide.

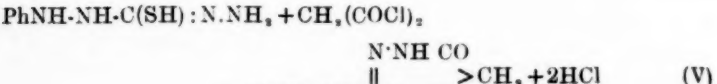


(III)

The action of six different acid chlorides, *viz.* acetyl chloride, benzoyl chloride, carbonyl chloride, phthalyl chloride, malonyl-chloride and thionyl chloride has been studied with the result that with the first three reagents, 1-phenylthiocarbohydrazide is only converted into its hydrochloride; with the last three however, there were obtained 2-phenylhydrazino-5-hydroxy-6:7-benzo-8-keto-1:3:4-octathiodiazine, 2-phenylhydrazino-5-hydroxy-6:7-dihydro-7-keto-1:3:4-thioheptadiazine and 2-phenylhydrazino-5-sulphoxy-1:5:3:4-dithiobiazole respectively, thus:



(IV)



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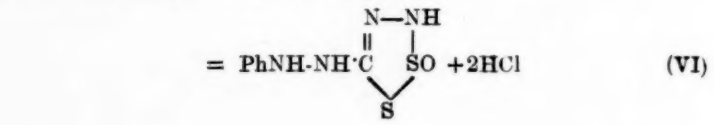
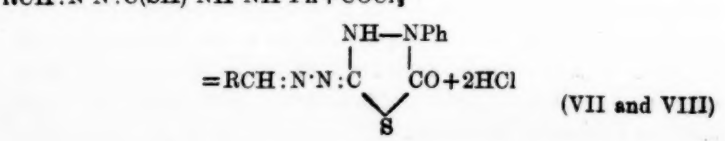


(VI)

Though phosgene was found to be of little use for the formation of heterocyclic compounds by reacting directly with 1-phenylthiocarbohydrazide, it has however been possible to make it react with benzal and *p*-nitro-benzal derivatives of the hydrazide to yield thiodiazole derivatives, thus:



(VII and VIII)

The formation of these closed-ring compounds is solely due to the fact that in its benzal- and *p*-nitrobenzal- derivatives the hydrazide has lost much of its basic character and it can no longer form any hydrochloride, which if once formed, as in the case of the free 1-phenylthiocarbohydrazide, does not show any tendency whatsoever to react further with acid chlorides.

Mono-substituted thiocarbohydrazides react with carbimides and thiocarbimides to form the corresponding carbophenylamides and carbothiophenylamides (*cf.* Guha and De, *loc. cit.*).

$PhNH{\cdot}NH.CS.NH.NH.CO{\cdot}NHPh$ ... (IX)

$PhNH{\cdot}NH.CS.NH{\cdot}NH.CS.NHPh$ ... (X)

$PhN(Me){\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NHPh$ ... (XI)

$CH_3{\cdot}C_6H_4NH.NH.CS.NH{\cdot}NH{\cdot}CS{\cdot}NHPh$ ... (XII)

The ring-closure of this type of lengthened chain-compounds has been effected with strong hydrochloric acid, potassium hydroxide solution and ferric chloride. Phenylthiocarbohydrazide-carbophenyl amide ($PhNH{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NHPh$) loses one molecule of sulphuretted hydrogen and yields 1-phenyl-2-phenylhydrazino-5-keto-4: 5-dihydro-1:3:4-triazole on being boiled with 20 per cent. potassium hydroxide solution, thus:

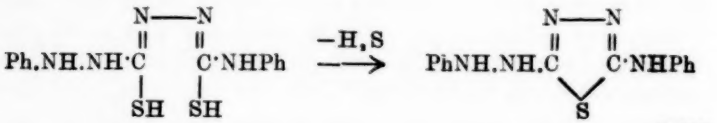
$$\begin{array}{l} NH\text{-}CO\text{-}NHPh \\ | \\ NH\text{-}CS.NH\text{-}NHPh \end{array} \xrightarrow{KOH} \begin{array}{l} NH.CO \\ | \qquad >NPh \\ N{=}{=}C{\cdot}NH{\cdot}NHPh \end{array} + H_2S$$

(XIII)

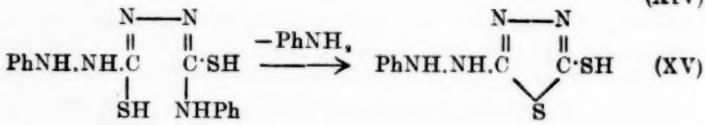
Arndt and Bielich (*Ber.*, 1922, **55**, 341) analogously obtained anilino-urazole from the hydrazide, $PhNH.CS.NH.NH.CO{\cdot}NH_2$, and phenylthiourazole and thiourazole from the hydrazide $PhNH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NHPh$ on treatment with sodium hydroxide solution.

Potassium hydroxide solution brings about the ring-closure of the dicarbothioamide $PhNH.NH{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NHPh$ to yield simultaneously two thiobiazole compounds. One is formed by the loss of one molecule of aniline and the other by the elimination of one molecule of sulphuretted hydrogen. The two products, *viz.*, 2-phenylhydrazino-5-anilino-1:3:4-thiodiazole and 2-phenylhydrazino-5-thiol-1:3:4-thiodiazole can be separated by taking advantage of the solublity in alkali of the latter by virtue of the thiol group present in it. The thiolthiodiazole readily forms a disulphide and

gives a triacetyl derivative. The thiodiazoles are formed according to the following scheme: --



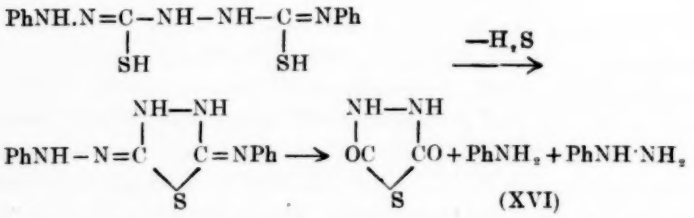
(XIV)



(XV)

Arndt and Milde (*Ber.*, 1921, **54**, 2089) obtained imino-thiol-triazoles from hydrazides of the type RNH·CS·NH·NH·CS·NHR (R = Ph, or H). It is noticeable that Arndt and Milde's compounds do not contain any sulphur in the ring. Guha and Guha obtained, however, 2-phenylimino-5-thiol-2:3-dihydro-1:3:4-thiodiazole (which contains an atom of sulphur in the ring) from phenylthiosemicarbazide-methyldithiocarboxylate. Evidently the present reaction combines in it both types of ring formation as studied by Arndt and Milde and by Guha and Guha.

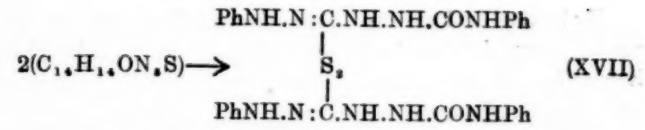
Concentrated hydrochloric acid acts upon the carbothiophenylamide (PhNH.NH.CS.NH.NH.CS.NHPh) to yield 2:5-diketo-1:3:4-thiodiazole, the formation of which can only be explained on the assumption that in the first stage 2-phenylhydrazino-5-phenylimino-1:3:4-thiodiazole is formed which yields the diketo-thiodiazole on hydrolysis, thus:—



(XVI)

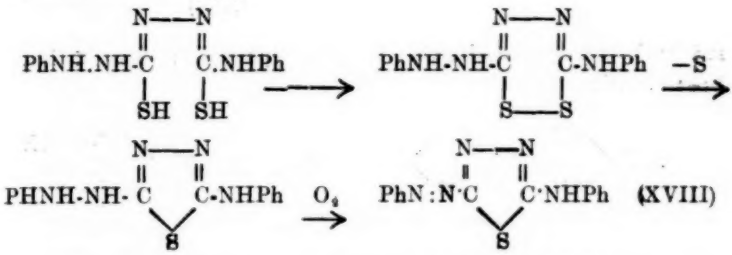
(*cf.* Freund and Imgart, *Ber.*, 1895, **28**, 949; Busch, Lotz and Schmidt, *J. pr. Chem.*, 1914, **90**, 57; *Ber.*, 1913, **46**, 2240; Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502).

Two molecules of phenylthiocarbohydrazide-carbophenylamide lose two atoms of hydrogen by the oxidising action of ferric chloride to yield a disulphide of the composition $C_{28}H_{22}O_2N_{10}S_2$:

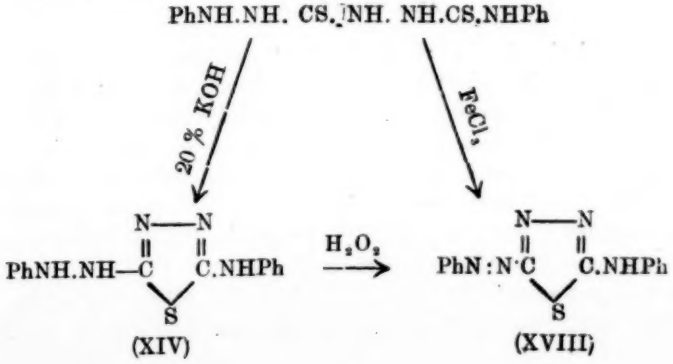


It appears peculiar that ferric chloride cannot act further upon this disulphide. Freund and Schander (*Ber.*, 1896, **29**, 2501) obtained a compound of the composition $C_4H_3N_3SO$, by the action of ferric chloride upon the hydrazide $NH_2CS.NH.NH.CO.NH_2$, which lost two atoms of hydrogen with one molecule of sulphuretted hydrogen.

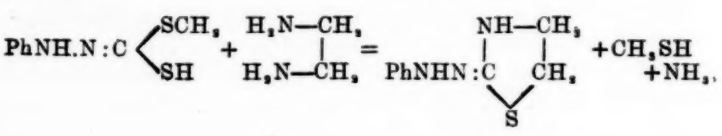
The action of ferric chloride upon the dithio compound, phenylthiocarbohydrazide-carbothiophenylamide proceeds similarly to that observed by Fromm (*Annalen*, **275**, 20; **433**, 1) with compounds of the type RNH.CS.NH.NH.CS.NHR, a thiobiazole derivative being formed thus:—



The intermediate compound which is identical with (XIV) cannot be isolated in this case as it gets instantaneously oxidised to the azo-compound (XVIII). This view has been further confirmed by the conversion of the compound (XIV) to the compound (XVIII) by oxidising with hydrogen peroxide. The following chart will make everything clear.

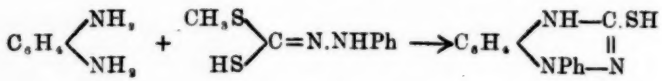


Hydrazine hydrate has been shown (Part III) to react with methyl-phenyldithiocarbazinate to yield methyl-phenylthiocarbohydrazide. It was expected that like hydrazine hydrate, ethylene and phenylenediamines might also react with the carbazinate to give open-chain compounds $C_6H_4(NH.CS.NH.NHPh)_2$ or $C_2H_4(NH.CS.NH.NHPh)_2$. But, peculiarly enough, methyl-phenyl-dithiocarbazinate has been found to react with the above diamines to yield different types of hetero-cyclic compounds. With ethylenediamine it gives 2-anilinamino-2:3:4:5-tetrahydro-1:3-thiazole,



(XIX)

and with *o*-phenylene-diamine it gives 1-phenyl-2:3-benzo-5-thiol-1:4:5-triazine, thus:



(XX)

The benzo-thiol-triazine is readily soluble in alkali and forms a disulphide and a monoacetyl derivative. A similar thiol-benzotriazine was prepared by Guha and Ray (*J. Indian Chem. Soc.*, 1925, 2, 81) by the action of potassium ethyl xanthate upon *o*-aminophenylhydrazine.

Experimental.

2-Phenylhydrazino-1:3:4-thiodiazole (I).—Phenylthiocarbohydrazide (2·5 g.) was heated with 10 c.c. of formic acid (100 per cent.) under reflux on a water-bath for 15 minutes when a clear solution was obtained which on cooling deposited a cake-like substance. It was powdered, washed with water and crystallised from alcohol in white plates, m.p. 220° with decomposition (yield almost quantitative). (Found: S, 16·92. $C_8H_8N_4S$ requires S, 16·69 per cent.). The compound is insoluble in acids and alkalis.

1-Phenyl-5-acetyl-thiocarbohydrazone (II.)—Phenylthiocarbohydrazide (2 g.) was covered with a sufficient quantity of acetic

anhydride when a clear solution was obtained with much evolution of heat. After some time, a crystalline precipitate separated out which was crystallised from alcohol in white rectangular plates. It shrinks at 168° and melts with decomposition at 172°-173°. It dissolves in alkali and can be precipitated by acids. (Found: N, 24·82. $C_9H_{12}ON_4S$ requires N, 25·00 per cent.).

On heating phenylthiocarbohydrazide with acetic anhydride and proceeding in the usual way, only a small quantity of the acetyl derivative could be isolated from the reaction mixture which consisted mainly of tarry matters.

Action of Potassium Ethyl xanthate: Formation of 2-Phenylhydrazino-5-thiol-1:3:4-thiodiazole (III).—A mixture of carbon bisulphide (2 g.) and 1-phenylthiocarbohydrazide (3·6 g.) dissolved in 20 c.c. of alcohol (containing 1·5 g. of KOH) was heated in a sealed tube at 100° for five hours. On cooling, crystals of the potassium salt deposited which were dissolved in water and the free acid obtained by acidification with hydrochloric acid. It was purified by dissolving in alkali and reprecipitating with acid. It was crystallised from hydrochloric acid, m.p. 127° with decomposition. (Yield 1 gm.). It tarnishes on exposure to the air. (Found: S, 28·82. $C_8H_8N_4S_2$ requires S, 28·48 per cent.).

The *disulphide* of compound (III) was prepared by boiling it with a solution of ferric chloride for about 15 minutes and crystallising the solid thus obtained from a large quantity of alcohol in red needles, m.p. 237° (with decomposition). (Found: S, 29·12. $C_{16}H_{14}N_8S_4$ requires S, 28·57 per cent.).

Action of Phosgene.—Phenyl-thiocarbohydrazide was suspended in benzene in a stoppered flask and the required quantity of phosgene (in toluene solution) was gradually added. The mixture was shaken for an hour and kept overnight with a lose cork. Next day, it was heated under reflux for a few minutes. The solid product thus separated was proved to be the hydrochloride of the base by preparing the benzaldehyde derivative as also by taking the mixed melting point.

Action of Acetyl Chloride.—The hydrazide was heated with acetyl chloride under reflux for about half an hour when a clear solution was obtained. On concentration a white solid was obtained and was proved to be the hydrochloride of the hydrazide.

Action of Benzoyl Chloride.—On being heated with benzoyl chloride in chloroform solution the thio-compound yielded the same hydrochloride.

2-Phenylhydrazino-5-hydroxy-6:7-benzo-8-keto-1:3:4-octathiodiazine (IV).—A mixture of phthalyl chloride (2 g.) and phenylthiocarbohydrazide (1·8 g.) was heated in benzene solution under reflux for ten minutes when a white solid separated which was filtered, washed with benzene and crystallised from acetic acid in white long plates. It assumes a slight reddish tinge at 185° and melts at 206° with decomposition (yield quantitative). It dissolves in alkali and can be precipitated by the addition of acids. (Found: S, 10·71. $C_{18}H_{12}O_2N_4S$ requires S, 10·25 per cent.).

2-Phenylhydrazino-5-hydroxy-7-keto-6:7-dihydro-1:3:4-heptathiodiazine (V).—Malonyl chloride (1·4 g.) was added to a benzene solution of phenylthiocarbohydrazide (1·8 g.) when a brown flocculent precipitate was formed which was filtered, washed with benzene and purified by dissolving in alkali and precipitating with acid, and repeating this process for several times; it was insoluble in almost all organic solvents. It melts at 201-202° with decomposition. (Found: N, 21·96. $C_{10}H_{10}O_2N_4S$ requires N, 22·40 per cent.).

2-Phenylhydrazino-5-sulphoxy-1:5:4:3-dithiobiazole (VI).—A benzene solution of thionyl chloride (1·2 g.) and phenylthiocarbohydrazide (1·8 g.) were heated under reflux for half an hour when the suspended solid went into solution. On cooling an amorphous solid separated out which was redissolved in benzene and filtered hot. On cooling, an amorphous mass separated again which was washed with alcohol and dried. It melts with decomposition at 220° and is insoluble in all other solvents, acids and alkalis. (Found: S, 28·48. $C_7H_5ON_4S_2$ requires S, 28·07 per cent.).

Action of Chlorides of Dibasic Acids upon Aldehyde-Phenyl Thiocarbohydrazones.

2-Benzalhydrazone of 4-Phenyl-5-keto-tetrahydro-1:3:4-thiodiazole (VII).—Benzaldehyde-1-phenylthiocarbohydrazone (2·7 g.) was suspended in benzene and to it the required quantity of phosgene (20 per cent. in toluene solution) was added. The mixture on being heated for an hour on the water-bath gave a clear solution. On cooling, a crystalline precipitate separated out which was recrystallised from benzene in white rectangular plates. It shrinks at 195° and melts at 204-205° (yield 1 gm.). (Found: N, 19·13. $C_{15}H_{11}ON_4S$ requires N, 18·94 per cent.).

2-Nitrobenzalhydrazone of 4-Phenyl-5-keto-tetrahydro-1 : 3 : 4-thiodiazole (VIII).—The method of preparation was the same as in the case of the preceding compound. The compound was crystallised from a mixture of alcohol and pyridine in yellow rectangular plates, m. p. 258°. (Found: N, 20·63. $C_{15}H_{11}O_3N_5S$ requires N, 20·52 per cent.).

ACTION OF MUSTARD OILS AND *iso*CYANATES.

Phenylthiocarbohydrazide-carbophenylamide (IX).—Phenylthiocarbohydrazide (1·8 g.) was heated under reflux with phenyl *iso*cyanate (1·2 g.) in alcoholic solution for a minute when an insoluble product separated out. This was washed with methyl alcohol to remove some admixed tarry matters and crystallised from acetic acid in white plates, m. p. 209° (with decomp.). It dissolves in alkali and is precipitated by acids. (Found: N, 23·42. $C_{14}H_{13}ON_5S$ requires N, 23·26 per cent.).

Phenylthiocarbohydrazide-carbothiophenylamide (X).—An alcoholic solution of phenylthiocarbohydrazide (2·7 g.) was heated under reflux with phenyl mustard oil (2·7 g.) for two minutes, and the separated solid was crystallised from a large quantity of alcohol; m. p. 173-174°. It dissolves in alkali and can be precipitated by acids. (Found: N, 21·98. $C_{14}H_{13}N_5S_2$ requires N, 22·08 per cent.).

Phenylmethyl-thiocarbohydrazide-carbothiophenylamide (XI).—An alcoholic suspension of phenyl-methyl-thiocarbohydrazide (0·4 g.) was heated with phenyl mustard oil (0·3 g.) under reflux for one hour and the solid thus obtained was crystallised from dilute pyridine in white plates, m. p. 219-220° with decomp. (Found: N, 21·34. $C_{15}H_{17}N_5S_2$ requires N, 21·14 per cent.).

m-*Tolylthiocarbohydrazide-carbothiophenylamide* (XII) was similarly prepared as the preceding compound and was crystallised from acetic acid in white rectangular plates, m. p. 160° with decomp. (Found: S, 19·68. $C_{15}H_{17}N_5S_2$ requires S, 19·34 per cent.).

1-Phenyl-2-phenylhydrazino-5-keto-4 : 5-dihydro-1 : 3 : 4-triazole (XIII).—Phenylthiocarbohydrazide-carbophenylamide (7 g.) was heated under reflux with 40 c. c. of 20 per cent. potassium hydroxide solution for half an hour when a solid mixed with a little oily matter separated from the solution. The oily matter was removed by passing steam and the solid was crystallised from dilute alcohol in white needles. It shrinks at 238° and melts at 244-245° (yield 0·5

gm.). It is insoluble in acids and alkalis. (Found: N, 26·12. $C_{14}H_{13}ON_3$ requires N, 26·22 per cent.).

2-Phenylhydrazino-5-anilino-1:3:4-thiodiazole (XIV) *and 2-Phenylhydrazino-5-thiol-1:3:4-thiodiazole* (XV).—Phenylthiocarbohydrazide-carbothiophenylamide (10 g.) was heated with 60 c. c. of 20 per cent. potassium hydroxide solution under reflux for half an hour when a deep black solution containing a red oily substance was obtained. The oil was removed by passing steam and was proved to be aniline. The solution on cooling yielded a fine white crystalline product (XIV) which was crystallised from water after animal charcoal treatment in white rectangular plates. It shrinks at 195° and melts at 199° (yield 1·0 gm.). It is readily soluble in hydrochloric acid. (Found: N, 24·58; S, 11·61. $C_{14}H_{13}N_5S$ requires N, 24·74; S, 11·31 per cent.).

Isolation of Compound (XV).—The mother-liquor was next acidified with hydrochloric acid when a flocculent precipitate appeared which was crystallised from a large quantity of alcohol in shining white plates, m.p. 258-259° (yield 2·5 gm.). (Found: N, 25·42; S, 28·93. $C_8H_8N_4S_2$ requires N, 25·00; S, 28·57 per cent.).

The *disulphide* was prepared by heating the thiol compound (XV) with an excess of ferric chloride solution for ten minutes and the separated solid mass was purified by dissolving in acetic acid and precipitating with water. Being insoluble, it could not be crystallised from any organic solvent. It shrinks at 195° and melts with decomposition at 205°. (Found: N, 25·47. $C_{16}H_{14}N_8S_4$ requires N, 25·08 per cent.).

The *triacetyl derivative* was prepared by heating the thiol compound with acetic anhydride for about 15 minutes. On cooling a crystalline product separated out which was washed with water and alcohol and dried, m.p. 206-207°. It is insoluble in alkali. (Found: N, 16·38. $C_{14}H_{14}O_3N_4S_2$ requires N, 16·00 per cent.).

Action of Hydrochloric Acid upon Phenylthiocarbohydrazide-carbothiophenylamide: Formation of 2:5-Diketo-tetrahydro-1:3:4-thiodiazole (XVI).—The thio compound (7 g.) on being heated with strong hydrochloric acid for one and a half hours went into solution with separation of sulphur. The filtered solution on neutralisation with sodium carbonate yielded a solid admixed with an oily matter which was removed by passing steam. The solid was crystallised from alcohol in white needles, m.p. 222°. (Found: N, 23·82; S, 27·69. $C_9H_6O_2N_4S$ requires N, 23·73; S, 27·11 per cent.).

Oxidation of Phenylthiocarbohydrazidecarbophenylamide with Ferric Chloride: Formation of (XVII).—The thio compound was heated with ferric chloride solution for about half an hour and the separated solid was crystallised from acetic acid in red needles, m.p. 198-199° with decomposition. It is insoluble in acid and alkali. (Found: N, 23·34; S, 11·48. $C_{28}H_{22}N_{10}S_2O_2$ requires N, 23·20; S, 11·02 per cent.).

Action of Ferric Chloride upon Phenylthiocarbohydrazidecarbothiophenylamide: Formation of 2-Anilino-5-phenylazo-1:3:4-thiodiazole (XVIII).

The carbothiophenylamide on being heated with an excess of ferric chloride solution for about half an hour, yielded a red coloured solid. The solid was freed from sulphur by washing with carbon bisulphide and was crystallised from a mixture of alcohol and pyridine in red needles, m.p. 256-257°. It is insoluble in acids and alkalis. (Found: S, 11·72. $C_{14}H_{11}N_5S$ requires S, 11·39 per cent.). This compound was also obtained when compound (XIV) was oxidised with hydrogen peroxide in alcoholic solution.

2-Phenylhydrazino-2:3:4:5-dihydro-1:3-thiazole (XIX).—Methylphenyldithiocarbazinate (6 g.) contained in a beaker was covered with a sufficient quantity of ethylene diamine when a violent reaction ensued with considerable evolution of heat. The mixture was then heated on a water-bath for a few minutes to complete the reaction. The separated solid was filtered, washed with alcohol and crystallised from pyridine, m.p. 223° (yield 1·5 gm.) It is insoluble in acids and alkalis. (Found: N, 21·58. $C_9H_{11}N_3S$ requires N, 21·76 per cent.).

1-Phenyl-2:3-benzo-5-thiol-dihydro-1:4:6-triazine (XX).—An intimate mixture of the carbazinate (7·2 g.) and *o*-phenylene diamine (4·3 g.) was heated in an oil-bath at 130-140° for three to four hours during which a peculiar pungent smell was emitted. The reaction mixture was cooled, dissolved in potassium hydroxide solution and steam was passed in to remove some tar formed during the reaction. The filtered solution was then neutralised with dilute hydrochloric acid and the white precipitate thus obtained was crystallised from acetic acid, m.p. 292-293° (yield 1·5 gm.). (Found: N, 17·34. $C_{13}H_{11}N_3S$ requires N, 17·43 per cent.).

The *acetyl derivative* was prepared in the usual manner and was crystallised from acetic acid, m.p. 203-204°. It dissolves readily in alkali and is precipitated by hydrochloric acid. (Found: N, 15·23. $C_{15}H_{13}ON_3S$ requires N, 14·84 per cent.).

The *disulphide* was prepared by boiling the thiol compound with ferric chloride and the yellow solid thus obtained was washed repeatedly with water and alcohol. It shrinks at 230° and does not melt even at 300°. (Found: S, 13·72. $C_{16}H_{10}N_6S_2$ requires S, 13·33 per cent.).

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Condition of Silver Chloride and other sparingly soluble Substances in Gelatine.

By A. C. Chatterji and N. R. Dhar.

There is considerable difference of opinion amongst colloid chemists regarding the condition of substances like silver chloride, silver bromide, lead iodide, mercuric iodide, and other sparingly soluble substances when formed in presence of gels like gelatine, agar-agar, starch etc. Many people seem to believe that these sparingly soluble substances exist in gels in the supersaturated condition. Thus Freundlich (" Colloid and Capillary Chemistry," English Translation, p. 734) states: " Silver chromate in gelatine is always in supersaturated solution." In previous papers (Chatterji and Dhar, *Trans. Faraday Soc.*, 1926, **72**, 23; *Kolloid Zeit.*, 1925, **35**, 2, 89 ; 1926 **40**, 97) we have emphasised and shown experimentally that the above view is incorrect and that these substances exist mainly in the colloidal state. We have proved from electric conductivity measurements of silver chromate in varying concentrations of gelatine that the observed conductivity is much less than the conductivity calculated on the assumption that silver chromate exists wholly as ions in gelatine. Moreover diffusion experiments show that silver chromate, lead iodide etc., formed in gelatine or agar have no appreciable velocity of diffusion.

From our experiments on the electric conductivity of saturated and supersaturated solutions of substances like calcium chloride, sodium acetate etc., we find that there is no break in the conductivity curve when we pass from the saturated to the supersaturated solution. In other words, there is no marked difference in the physical properties of saturated and supersaturated solutions of electrolytes. Several years ago W. Ostwald (" Solutions " p. 59, 1891) stated: " That the electrical conductivity suffers no irregular change when the point of saturation is passed has been shown by C. Heim." Consequently it is difficult to understand how substances like silver chloride, silver chromate etc., can remain in the supersaturated condition in gelatine, because these substances when formed in gelatine do not show much electric conductivity.

The objection may be raised that in presence of the viscous medium gelatine or agar-agar, the electric conductivity will be

greatly decreased due to the viscosity of the medium ; but Arrhenius proved long ago that electric conductivity of substances like HCl, HNO_3 etc., when set in gelatine is practically the same as in aqueous solution of the same concentration under otherwise identical conditions.

In order to throw further light on the condition of sparingly soluble substances in gels we have carefully determined the electric conductivity of silver chloride formed in gelatine.

Experiments were undertaken to find out the conductivity of different amounts of silver chloride in gelatine of varying strengths at 35.°

Kahlbaum " Golddruck " gelatine was further purified by precipitating it from an aqueous solution by the addition of absolute alcohol. It was then dried at 85° and dissolved in conductivity water. This solution of gelatine was further freed from electrolytes by dialysis for a week until it showed no turbidity with silver nitrate.

The conductivity of the gelatine solution increased slightly with time on keeping and hence after each set of experiments the solution was dialysed for a day, and used for subsequent experiments after a fresh determination of the electric conductivity.

As silver chloride was obtained by the addition of equivalent quantities of silver nitrate and potassium chloride, an equivalent amount of potassium nitrate was also produced. In order to ascertain the conductivity of silver chloride alone, the conductivity of an equivalent concentration of potassium nitrate in gelatine was determined under identical conditions.

A typical result of the conductivity experiments is shown in Table 1.

TABLE I.

Concentration of gelatine	1·087	grm. in 100 c.c
Concentration of silver nitrate, potassium chloride etc.	N/800	
Conductivity of water at 35°	$2·5 \times 10^{-6}$	mhos.
Conductivity of gelatine	$0·279 \times 10^{-3}$	,,
Conductivity of gelatine and silver nitrate ...	$0·387 \times 10^{-3}$	,,
Conductivity of gelatine and potassium chloride	$0·481 \times 10^{-3}$	,,
Conductivity of gelatine, silver chloride and potassium nitrate	$0·4834 \times 10^{-3}$	,,
Conductivity of gelatine and potassium nitrate	$0·4821 \times 10^{-3}$	,,
Hence observed conductivity of silver chloride	$0·0013 \times 10^{-3}$	,,

Exactly similar results were obtained with other concentrations of silver chloride and gelatine and the results obtained are summarised in Table II.

TABLE II.

Concentration of silver chloride.	Concentration of gelatine.	Conductivity observed. (mhos).	Conductivity as calculated from the experiments assuming AgCl to be in the ionic condition (Mhos).	Conductivity observed expressed as percentage of calculated conductivity.
N/800	1·1%	$0·0013 \times 10^{-3}$	$0·1068 \times 10^{-3}$	0·84
N/400	,,	$0·0052 \times 10^{-3}$	$0·2839 \times 10^{-3}$	1·8
N/320	,,	$0·0187 \times 10^{-3}$	$0·4986 \times 10^{-3}$	3·9
N/160	,,	$-0·042 \times 10^{-3}$	$0·8026 \times 10^{-3}$	...
N/106·6	,,	$-0·417 \times 10^{-3}$	$1·2955 \times 10^{-3}$	...
N/800	0·64%	$0·0027 \times 10^{-3}$	$0·1477 \times 10^{-3}$	1·1
N/160	3·45%	$-0·0140 \times 10^{-3}$	$0·5600 \times 10^{-3}$	...
N/80	,,	$-0·0374 \times 10^{-3}$	$1·320 \times 10^{-3}$	...
N/53·3	,,	$-0·0650 \times 10^{-3}$	$2·116 \times 10^{-3}$	...
N/160	3·15%	$-0·0850 \times 10^{-3}$	$0·384 \times 10^{-3}$	...
N/106·6		$-0·085 \times 10^{-3}$	$0·745 \times 10^{-3}$	...

From the conductivity measurements given in Table I, the conductivity of silver chloride as determined by experiments can be ascertained by simply subtracting the conductivity of potassium nitrate from that of the mixture of silver chloride and potassium nitrate. If it is supposed that silver chloride remains in the ionic condition and not in the colloidal state, then its conductivity should be equal to the sum of the conductivities of silver nitrate and potassium chloride less the conductivity of potassium nitrate. Table II contains the results calculated on the basis of the above considerations.

From Table II it will be evident that if silver chloride were present in the ionic condition, the conductivity of this substance would have been much greater than the values actually obtained. As a matter of fact in the majority of the cases investigated the minus sign in the column of observed conductivity indicates that the conductivity of a mixture of silver chloride and potassium nitrate is less than the conductivity of potassium nitrate alone. As the

amount of silver chloride present in these experiments is sufficiently large, it seems that silver chloride in the course of its formation adsorbs some potassium nitrate, thereby lowering its effective concentration. Thus from our experimental results it will be seen that when the concentration of silver chloride is varied from N/160 to N/53·3 we always get appreciable adsorption of potassium nitrate by silver chloride causing negative value in the observed conductivity. On the other hand, when more dilute solutions of silver nitrate are used and when the concentration of AgCl varies from N/800 to N/266·6, the observed conductivity is positive, because the amount of adsorption of potsssium nitrate is less than in those experiments where more concentrated solutions of silver nitrate were used.

Hence the foregoing experimental results lead us to the conclusion that silver chloride formed in gelatine by the reaction of silver nitrate and potassium chloride exists in the colloidal state.

In order to corroborate our experiments with silver chromate in gelatine published in a previous paper we have carried on numerous experiments with gelatine of known conductivity in which silver chromate was allowed to form by the interaction of potassium chromate and silver nitrate and the following results were obtained.

TABLE III.

	Concentration of silver chromate.	Concentration of gelatine.	Conductivity observed (mhos.)	Conductivity calculated on the assumption that Ag_2CrO_4 is in the ionic condition (mhos.)	Observed conductivity expressed as percentage of calc. conductivity.	Conductivity of gelatine (mhos.)
1	N/100	3%	$0·1425 \times 10^{-3}$	$0·8010 \times 10^{-3}$	17·7%	$0·4786 \times 10^{-3}$
2	N/500	3%	$0·1310 \times 10^{-3}$	$0·3022 \times 10^{-3}$	43·2%	$0·5106 \times 10^{-3}$
3	N/120	3·25%	$0·1833 \times 10^{-3}$	$0·5772 \times 10^{-3}$	31·7%	$0·3300 \times 10^{-3}$
4	N/700	3·25%	$0·0156 \times 10^{-3}$	$0·0532 \times 10^{-3}$	29·3%	$0·4630 \times 10^{-3}$
5	N/280	2·75%	$0·2455 \times 10^{-3}$	$0·7453 \times 10^{-3}$	32·8%	$0·6022 \times 10^{-3}$
6	N/400	2·6%	$0·1347 \times 10^{-3}$	$0·2809 \times 10^{-3}$	47·9%	$0·6716 \times 10^{-3}$
7	N/320	2·6%	$0·0153 \times 10^{-3}$	$0·1520 \times 10^{-3}$	10·1%	$1·2766 \times 10^{-3}$ (undialysed).
8	N/106·8	2·6%	$0·156 \times 10^{-3}$	$0·8010 \times 10^{-3}$	19·4%	$1·790 \times 10^{-3}$ (undialysed).
9	N/320	8·15%	$0·0095 \times 10^{-3}$	$0·1805 \times 13^{-3}$	5·2%	$1·563 \times 10^{-3}$
10	N/160	8·15%	$0·1245 \times 10^{-3}$	$0·6485 \times 10^{-3}$	19·0%	$1·535 \times 10^{-3}$

The conductivity of the water used $= 2·5 \times 10^{-6}$ mhos. at 35°

In Table XIV of their paper Bolam and Mackenzie (*Trans. Faraday Soc.*, 1926, **67**, 160) point out that "the amount of silver other than ion is directly proportional to the gelatine concentration." The following table which is taken from their paper will illustrate their conclusion.

TABLE IV.

$Ag-Ag^{\circ}$ Normality $\times 10^5$	Gelatine per cent.	$\frac{Ag-Ag^{\circ}}{\text{Gelatine concentration}}$
(333−108)	3·0	$\frac{333-108}{3}=75\times10^{-5}$
(236−106)	1·59	$\frac{236-106}{1\cdot59}=82\times10^{-5}$
(162−108)	0·70	$\frac{162-103}{0\cdot70}=77\times10^{-5}$

They obtained the above table from the results recorded in Table II. of their paper where only the minimum quantity of gelatine necessary to prevent precipitation was present. But if we calculate the relationship between the amount of silver other than ion and the gelatine concentration from the results recorded by Bolam and Makenzie in Table V of their paper where the concentrations of gelatine as well as of silver chromate were widely varied we get results which are given in the following table. The mean value obtained from the *E. M. F.* data in the final reading has been taken to indicate the amount of silver present as ion.

TABLE V.

$Ag-Ag^{\circ}$ Normality $\times 10^5$	Gelatine per cent.	$\frac{Ag-Ag^{\circ}}{\text{Gelatine concentration}}$
(333−108·4)	3·0	$74\cdot86\times10^{-5}$
(250−68)	3·0	$66\cdot67\times10^{-5}$
(125−14·5)	3·0	$37\cdot17\times10^{-5}$
(236−106·8)	1·59	$81\cdot26\times10^{-5}$
(118−35·9)	1·59	$51\cdot63\times10^{-5}$
(324−66)	0·70	$368\cdot57\times10^{-5}$
(162−108)	0·70	$77\cdot14\times10^{-5}$
(333−35·7)	6·00	$49\cdot66\times10^{-5}$
(333−59·7)	4·50	$60\cdot73\times10^{-5}$
(236−50·3)	3·17	$58\cdot58\times10^{-5}$
(236−83·7)	2·11	$72\cdot18\times10^{-5}$
(236−134·2)	1·06	$96\cdot03\times10^{-5}$
(162−41)	2·1	$57\cdot61\times10^{-5}$
(162−67·2)	1·4	$67\cdot71\times10^{-5}$
(162−117·7)	0·35	$126\cdot57\times10^{-5}$

From the above table it will be at once evident that there exists no definite relation between the amount of silver that is present other than in the ionic condition and the quantity of gelatine in the solution.

Moreover, it is apparent from the results obtained by Bolam and Mackenzie that the quantity of silver present as ion calculated from the *E.M.F.* data is much less than the total amount of silver present. The following table which is obtained from the results of Bolam and Mackenzie given in their Table V shows the relation between the total amount of silver and the quantity present as ion.

TABLE VI.

Concentration of gelatine in per cent.	Total amount of silver. Normality $\times 10^5$	Amount of silver as ions. Normality $\times 10^5$	Percentage of silver present as ions.
3	333	108·4	32·6
3	250	68·0	27·2
3	125	14·5	11·6
1·59	236	106·8	45·2
1·59	118	35·9	30·4
0·70	324	66·0	20·4
0·70	162	108·0	66·6
6·0	333	35·7	10·7
4·5	333	59·7	17·9
3·0	333	108·4	32·6
1·5	333	104·8	31·5
1·0	333	74·6	22·4
3·17	236	50·3	21·3
2·11	236	83·7	35·3
1·59	236	106·2	45·0
1·06	236	134·2	56·8
1·06	236	82·6	33·6
1·06	236	67·8	28·7
2·10	162	41·0	25·3
1·4	162	67·2	41·4
0·70	162	108·2	66·6
0·35	162	117·7	72·6
0·35	162	65·2	40·2

From the above table it will be clear that the amount of silver present as ion is in the majority of cases less than 40% of the total silver; or in other words, nearly two thirds of the silver exists in a form other than ionic.

We are of the opinion that the two thirds of the silver, which does not exist in the ionic condition, remain in the colloidal state. Hence the measurements of Bolam and Mackenzie are in support of our views that the sparingly soluble substance formed in presence of gelatine exists as a colloid. Moreover it should be emphasised that the hydrogen ions present in gelatine exert a solvent action on the silver chromate formed, because silver chromate dissolves in acids and hence more free silver ions are detected in the solution due to the existence of hydrogen ions in gelatine. In the case of silver chloride the hydrogen ions present in gelatine cannot dissolve silver chloride and hence the amount of free silver ions present with silver chloride is much less than the amount found in the case of silver chromate.

Summary and Conclusion.

(1) Measurements of electrical conductivity of silver chloride of different concentrations in gelatine prove that the observed conductivity is much less than the conductivity calculated on the assumption that silver chloride exists wholly as ions in gelatine.

Exactly similar results have been obtained with silver chromate in gelatine.

(2) From the experimental results of Bolam and Mackenzie with silver chromate in gelatine it can be concluded that there exists no definite relationship between the amount of silver present in the non-ionic condition and the quantity of gelatine present. Their experiments on *E.M.F.* measurements shew that the amount of silver present in the ionic condition in silver chromate in gelatine is approximately 40 per cent.

(3) In the case of silver chloride the hydrogen ions present in gelatine cannot dissolve silver chloride and hence the amount of free silver ions present with silver chloride is much less than in the case of silver chromate in gelatine.

(4) Our experimental results show that silver chloride, silver chromate etc., formed in gelatine exist mainly in the colloidal state.

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Photo-bromination of *m*-Nitrobenzylidene Malonic Ester. Part II.

By

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In a previous paper (This *Journal*, 1927, **4**, 375) the photo-bromination of *m*-nitrobenzylidene malonic ester in carbon tetrachloride solutions has been studied. The present investigation deals with the same reaction with carbon disulphide as the solvent. It might be mentioned at the outset that the main features of this investigation are exactly analogous to those previously obtained. As before, a photo-chemical equilibrium ensues which is given by *Dibromide/Bromine* × *Ester*, and which again is determined by temperature and intensity of radiation. The equilibrium once attained does not change when the system in equilibrium is transferred to darkness.

Experimental.

The methods of investigation were the same as before. The incident radiation was measured by means of a Moll thermopile and a Moll galvanometer. The dark reaction was found to be negligible there being practically no reaction in course of 24 hours.

Tables I-IV indicate the result of the experiment on the determination of the point of equilibrium.

Table I.

Intensity of light (488·5$\mu\mu$)—160/12 Hefners-at-100 cm.

Temperature 32°.

Initial conc. of ester : gm. mol./litre.	Initial conc. of bromine : gm. mol./litre.	Equilibrium conc. of Br : gm. mol./litre.	Dibromide / Bromine × Ester.
·0150	·0150	·00875	81·6
·0100	·0100	·0066	79·2
·0067	·00685	·00505	78·0
·0050	·0049	·00375	80·1
·0150	0096	·00530	75·8
·0100	·01495	·01045	78·3
		Mean	78·0

TABLE II.

Intensity of incident light (488·5 $\mu\mu$)—77/12 Hefners-at-100 cm.

Temperature 32°.

Initial conc. of ester : gm. mol./litre.	Initial conc. of Br : gm. mol./litre.	Equilibrium conc. of Br : gm. mol./litre.	Dibromide Bromine × Ester.
·0150	·0152	·0102	49·0
·0100	·0097	·0072	48·8
·0067	·0067	·00525	52·4
·0067	·00955	·00765	51·6
·0100	·00725	·00525	49·0
·0050	·0050	·00415	49·7
		Mean	50·0

TABLE III.

Intensity of light (488·5 $\mu\mu$)—160/12 Hefners-at-100 cm.

Temperature 27°.

Initial conc. of ester : gm. mol./litre.	Initial conc. of Br: gm. mol./litre.	Equilibrium conc. of Br : gm. mol./ litre.	Dibromide Bromine × Ester.
·0150	·01495	·0094	62·4
·0102	·0096	·0067	59·3
·0067	·0065	·00505	54·7
·0050	·0049	·00395	59·4
		Mean	58·9

TABLE IV.

Intensity of incident light (488·5 $\mu\mu$)—77/12 Hefners-at-100 cm.

Temperature 27°.

Initial conc. of ester : gm. mol./litre.	Initial conc. of bromine : gm. mol./litre.	Equilibrim conc. of Br : gm. mol./litre.	Dibromide Bromine × Ester .
·0150	·01410	·0100	38·2
·0100	·0097	·0075	37·6
·0067	·0071	·00585	38·9
·0005	·0049	·0042	36·2
		Mean	37·7

Comparison of Tables I and II and Tables III and IV again brings out the interesting fact that the ratio of the equilibrium constants 1·55 (78/50 and 59/78) is equal to the ratio of the square root of the corresponding incident intensities $\sqrt{160/77}=1\cdot45$.

Experiments on the Rate of Bromination.

In this investigation the initial concentrations of ester and bromine were not always identical and the velocity of bromination should, therefore, be given by

$$\frac{dx}{dt}=k_1(a-x)(b-x)-k_2x \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where a and b represent the initial concentrations of ester and bromine respectively.

Integration of this equation gives

$$k_1=\frac{1}{t}\,\frac{1}{c_2-c_1}\left[\log\frac{c_2-x}{c_2}-\log\frac{c_1-x}{c_1}\right]$$

where c_1 and c_2 are the roots of the equation,

$$ab-x\left(a+b+\frac{k_2}{k_1}\right)+x^2=0$$

i.e., c_1 is the equilibrium value of x, and $c_2=\dfrac{ab}{c_1}$

when $a=b$, the roots are

$$a+\lambda+\sqrt{\lambda\,(2a+\lambda)} \text{ and } a+\lambda-\sqrt{\lambda(2a+\lambda)} \text{ where } \frac{1}{2\lambda}=\frac{k_1}{k_2},$$

and in that case

$$k_1=\frac{1}{t}\,\frac{1}{2\sqrt{\lambda(2a+x)}}\left[\log\frac{a+\lambda-x+\sqrt{\lambda(2a+\lambda)}}{a+\lambda-x-\sqrt{\lambda(2a+\lambda)}}\right.$$

$$\left.-\log\frac{a+\lambda+\sqrt{\lambda(2a+\lambda)}}{a+\lambda-\sqrt{\lambda(2a+\lambda)}}\right] \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

which is the equation used in Part I.

Tables V to VIII indicate the typical results and Table IX gives a summary of all the measurements, One c. c. of the reaction mixture was titrated throughout.

TABLE V (SERIES A, TABLE IX).

Intensity of incident light (488·5 $\mu\mu$)—160/12 Hefners-at-100 cm. Conc. of ester—0·0150 *M*. Conc. of bromine—0·0096 *M*.

Temperature 32°.

Time in minutes.	N/500 bromine.	k_1	Mean k_1
0	9·60 c. c.	...	
60	8·60	·134	
120	7·85	·134	·136
210	6·90	·138	

TABEL VI (SERIES B, TABLE IX).

Intensity of incident light (488·5 $\mu\mu$)—77/12 Hefners-at-100-cm.

Temperature 32°.

Conc. of ester—0·0067 *M*. Conc. of bromine—0·0067 *M*.

Time in mins.	N/500 bromine.	k_1	Mean k_1
0	6·7 c. c.		
60	6·45	·102	
120	6·25	·102	·102
210	6·0	·101	

TABLE VII (SERIES C, TABLE IX).

Intensity of incident light (488·5 $\mu\mu$)—160/12 Hefners-at-100 cm.

Temperature 27°.

Conc. of ester—0·0150 *M*. Conc. of bromine—0·01495 *M*.

Time in mins.	N/500 bromine.	k_1	Mean k_1
0	14·95 c. c.	...	
60	13·8	·097	
120	12·9	·098	·100
210	11·75	·106	

TABLE VIII (SERIES D, TABLE IX).

Intensity of incident light (488·5$\mu\mu$)—77/12 Hefners-at-100 cm.

Temperature 27°.

Conc. of ester—0·0150 M. Conc. of bromine—0 0149 M.

Time in mins	N/500 bromine	k_1	Mean k_1
0	14·1 c.c.		
60	13·3	·0706	
120	12·7	·0684	·0700
180	11·7	·0712	

TABLE IX.

Series	Intensity of radiation.	Temperature.	Initial conc. of ester.	Initial conc. of Br.	Mean k_1
A	160/12 Hefners-at −100 cm.	32°	·0150 M	·0150 M	·127
			·010 M	·0101 M	·137
			·0067 M	·00685 M	·136
			·0150 M	·0096 M	·138
			·010 M	·01495 M	·127
B	77/12 Hefners-at −100 cm.	32°	·0150 M	·0152 M	·0924
			·010 M	·0097 M	·0900
			·0067 M	·0067 M	·102
			·0067 M	·00955 M	·0900
C	160/12 Hefners-at −100 cm.	27°	·0150 M	·01495 M	·100
			·0102 M	·0096 M	·0922
			·0067 M	·0065 M	·1027
D	77/12 Hefners-at −100 cm.	27°	·0150 M	·0140 M	·0700
			·010 M	·0097 M	·0597
			·0067 M	·0071 M	·0672

It will be seen that, as before, intensity of radiation and temperature remaining constant, the value of k_1 remains the same.

Temperature Coefficient of k_1 and k_2.

Comparison of series A and C and Series B and D of measurements gives the values

$$\left(\frac{\cdot 133}{\cdot 0983}\right)^{\frac{10}{5}} \text{ i.e. } 1{\cdot}8 \text{ and } \left(\frac{\cdot 096}{\cdot 0659}\right)^{\frac{10}{5}}$$

i.e. 2·1 for the temperature coefficient of k_1. We can now calculate the temperature coefficient of k_2. Let x be the temperature coefficient of k_2 for 5°C (32°—27°).

Now at 27° from Table III, $K_1 \left(\frac{k_1}{k_2}\right) = 59{\cdot}0$

K_2, the equilibrium constant at 32° = 78·0 (*vide* Table I).

$$\text{Again } K_2 = \frac{k_1 \text{ at } 27° \times 1{\cdot}4}{k_2 \text{ at } 27° \times x}$$

$$= K_1 \times \frac{1{\cdot}4}{x} \quad \text{or } x = 1{\cdot}06.$$

Therefore, the temperature coefficient of k_2 for 10°C

$= 1{\cdot}06^{\frac{10}{5}} = 1{\cdot}12$ a value less than that for k_1.

Application of Einstein's Law.

The reverse reaction during the first 60 minutes will not be very great and we can approximately calculate the quantum efficiency. Taking the results in Table VII, since the absorption of the incident radiation (488·4 $\mu\mu$) by bromine solutions in carbon disulphide employed can be taken to be complete, number of quanta absorbed per square cm per second

$$= \frac{160}{12} \times 900 \frac{488 \times 10^{-7}}{3 \times 10^{10}} \times \frac{1}{6{\cdot}5 \times 10^{-27}}$$

$= 3{\cdot}0 \times 10^{15}$ quanta per sq. cm. per sec.

The change is 1·15 c.c. N/500 bromine per c.c. in 60 minutes; hence no. of mols transformed per sq. cm. per sec. × depth of reaction vessel

$$= \frac{1{\cdot}15}{1000 \times 1000} \times \frac{1}{60 \times 60} \times 6{\cdot}1 \times \quad \times 1{\cdot}5 \text{ (depth of reaction vessel)}$$

$= 0{\cdot}28 \times 10^{15}$ mols per sq. cm. p. r sec.

Thus about 11 quanta are necessary for the transformation of one molecule. When calculated, the quantum efficiency in all cases comes out to be less than unity.

Theoretical.

Since the first part of the paper was published, a paper by Berthoud and Nicolet on the photo-bromination of the nitrile of α-phenylcinnamic acid has appeared in *Helvetiaca Chimica Acta* (1927, **10**, 417). These authors maintain that the velocity of photo-bromination in this case is proportional to the concentration of bromine and is independent of the concentration of the nitrile, while the velocity of the reverse decomposition is proportional directly to the concentration of the dibromide and inversely to the concentration of the nitrile. They thus obtain the following equation.

$$\frac{d[ABr_2]}{dt} = k_1[Br_2] - k_2 \frac{[ABr_2]}{A} \qquad \ldots \quad (3)$$

which gives for zero velocity, when photochemical stationary state has been reached, the mass action expression,

$$\frac{[A][Br_2]}{[ABr_2]}=K$$

This costant is obviously independent of the intensity of illumination.

It is clear that our experiments on the photo-bromination of *m*-nitrobenzylidene malonic ester yield results which must be interpreted in a different way. In the first place, the equilibrium constant has been found to depend on the intensity of illumination, being in fact proportional approximately to the square root of the intensity of incident light. Again as the following measurements in carbon tetrachloride solutions (*vide* Table X) will show, the velocity of photobromination at the initial stage of the reaction, where the effect of the reverse reaction can be neglected without involving much error, is not only proportional to the concentration of bromine but increases very considerably as the concentration of the ester reases.

TABLE X.

Temperature 32°.

Conc. of ester ...	·0040M	·0067M	·0067M	·0133M
Conc. of bromine ...	·00815M	·0080M	·00665M	·0067M
Change of Br conc. in first 20 mins. in c. c. N/500 sol. per c.c. of mixture.	0·35 c.c.	0·65 c.c.	0·50 c.c	0·75 c.c.

It is evident that equation (3) as given by Berthoud is not applicable to this reaction. It appears almost impossible to ignore the fact that whenever photobromination does not proceed to completion the concentrations of the unsaturated molecule and the dibromide affect very considerably the velocity of bromination or reverse decomposition. In the particular reaction we have studied, the results can be expressed within certain ranges of concentration by the equation,

$$\frac{d[ABr_2]}{dt}=k_1[A][Br_2]\,I-K_2\sqrt{1}[ABr_2$$

Influence of Solvent: It will be seen by referring to Tables III and IV of the previous paper (*loc. cit.*) and Tables II and IV of this

paper that for the same intensity of incident radiation the value of the equilibrium constant in carbon tetrachloride solutions is about seven times the value of the constant in carbon disulphide solutions. The velocity of bromination in carbon tetrachloride is also about seven times the corresponding value for carbon disulphide solutions (*vide* Tables V and VI of Part I and Tables X-XIII of this paper). Thus in carbon disulphide solutions the reverse reaction, *i.e.*, the decomposition of the dibromide proceeds further and more quickly than in carbon tetrachloride solutions.

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Extinction Coefficient of Mixtures of Ferric Chloride and Organic Acids in the Ultraviolet as experimental Evidence in Favour of the Formation of unstable Intermediate Compounds. Part II.

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In a previous paper (*J. Indian Chem. Soc.*, 1927, **4**, 353) it has been shown that the observed exaltation in the values of extinction coefficients, when uranyl salt is mixed with organic acids, can be explained quantitatively on the hypothesis that an intermediate compound is produced by the association of one molecule of uranyl salt with one molecule of organic acid. The dissociation constant of this intermediate compound and its extinction coefficients for several wave-lengths in the ultraviolet were calculated according to a method developed in that paper.

It is well known that almost all organic acids are oxidised by ferric salts in presence of light; and it was felt that investigations on lines developed in the previous paper might decide if the photochemical oxidation observed with ferric salts is preceded by the formation of an intermediate compound which undergoes decomposition by the action of light resulting in the reduction of the ferric radical and the simultaneous oxidation of organic part of the complex molecule.

The experimental procedure and the methods of calculation are identical with those described before; from the tables given in this paper, it will be seen that the experimental data on the extinction coefficient of mixtures can be quantitatively explained on the basis of—

(1) An equilibrium in solution between the ferric salt and organic acid as reactants and an intermediate complex formed by the loose combination of one molecule each of the reactants.

(2) The assumption of a definite value of molecular extinction coefficients for each wave-length for the intermediate complex so formed.

Experimental.

A ferric chloride solution of strength N/500 was made by dissolving the requisite quantity of sublimed $FeCl_3$ (Merck) in N/10 HCl. The solution was subsequently standardised (strength 1·003N/500). The factor was ignored in all the calculations.

The purity of hydrochloric acid used was tested by comparing the absorption spectrum o/f N10 HCl with that of water.

The organic acids were carefully purified in the laboratory.

The extinction coefficients of a dilute solution of ferric chloride and of acid solutions of various concentrations were determined separately and compared with the values of extinction coefficients of mixtures.

The concentration of the salt (both uranyl nitrate and ferric chloride) is a factor of very great importance. It is found that regularities in exaltation of the extinction coefficients of the mixtures are to be met with, only in a very dilute solution of the inorganic salt within ranges of concentration for which Beer's Law actually holds good.

The observations were always made with mixtures of salt and organic acid, where the acid was in excess, the ratio of acid-salt being in no case less than 10.

Table I.

M/6000 *Ferric Chloride* (*F*) *and Formic Acid.* $K=18$.

Log I_0/I_t = Extinction coefficient (E).

(—) Indicates that the extinction coefficient is negligibly small.

Wave-length	2961	2770	2600	2445	Conc. of intermediate complex (x), as calc.
M/6000 (F) E obs. ...	·25	·35	·75	·9	
M/5 acid, E obs. ...	—	—	—	·3	
Mixture (M/5 acid and M/6000 F) E obs.	·5	·85	1·00	1·50	$·130 \times 10^{-3}$
E calc.	·55	·84	1·01	1·50	
M/10 acid, E obs. ...	—	—	—	·15	
Mixture (M/10 acid and M/6000 F) E obs.	·50	·75	·95	1·30	107×10^{-3}
E calc.	·49	·75	·96	1·29	
M/20 acid, E obs. ...	—	—	—	·05	
Mixture (M/20 acid and M/6000 F) E obs.	·40	·65	·90	1·10	$·079 \times 10^{-3}$
E calc.	·43	·65	·91	1·13	

Wave-lenght	2961	2770	2600	2445	Conc. of intermediate complex (x), as calc.
M/50 acid, E obs. ...	—	—	—	—	
Mixture (M/50 acid and M/6000 F) E obs. ...	·35	·50	·85	1·00	$·044 \times 10^{-3}$
E calc.	·35	·51	·84	1·00	
M/100 acid. E obs. ...	—	—	—	—	
Mixture (M/100 acid and M/6000 F) E obs. ...	·30	·45	·80	·95	$·075 \times 10^{-3}$
E calc.	·31	·45	·80	·96	

In calculating the values of E for the various mixtures K has been assumed to be 18 in all the cases and E_M^{λ} (molecular extinction coefficient of the intermediate complex) given the following values for various wave-lengths—

λ ...	2961	2770	2600	2445
E_M ...	$1·14 \times 10^3$	$1·86 \times 10^3$	$·99 \times 10^3$	$1·14 \times 10^3$

With M/3000 conc. of ferric chloride and varying concentrations of formic acid, extinction coefficients could be measured for longer wave-lengths and the ovserved values of extinction coeffs. for mixtures could be reproduced by assuming $K=18$ and

λ ...	3364	3274	2961	2470
E_M ...	$·57 \times 10^3$	$·78 \times 10^3$	$1·14 \times 10^3$	$1·84 \times 10^3$

TABLE II.

M/6000 *Ferric Chloride* (F) *and Acetic Acid.* $K=11$.

Wave-length	*Log.* I_o/I, 3274	2961	2770	2445	x Calc.
M/6000 F ...	·20	·25	·35	·90	
M/acid ...	—	—	—	1·50	
Mixture ...	·45	·75	·75	...	$·153 \times 10^{-3}$
E calc. ...	·46	·71	·74		
M/5 acid ...	—	—	—	·30	
Mixture ...	·40	·60	·65	1·40	$·115 \times 10^{-3}$
E calc. ...	·39	·59	·65	1·40	
M/10 acid ...	—	—	—	·15	
Mixture ...	·35	·50	·55	1·20	$·087 \times 10^{-3}$
E calc. ...	·36	·51	·57	1·20	

Wave-length.		3274	2961	2770	2445	x Calc.
M/20 acid	...	—	—	—	·10	
Mixture	...	·30	·45	·50	1·10	·059 × 10^{-3}
E calc.	...	·30	·43	·50	1·10	
M/50 acid.	...	—	—	—	—	
Mixture	...	·25	·35	·45	·95	·030 × 10^{-3}
E calc.	...	·25	·34	·43	·9[illegible]	
		E_M — ·84 × 10^3	1·50 × 10^3	1·29 × 10^3	·85 × 10^3	

In calculating the values of E for the various mixtures K has been assumed to be 11, and the above values of E_M^{λ} given.

With M/3000 conc. of ferric chloride and varying concentrations of acetic acid, extinction coefficients could be measured for higher wave-lengths and the observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=11$ and

λ	...	3435	3364	3274	2961	2770
E_M	...	·63 × 10^3	·86 × 10^3	·86 × 10^3	1·54 × 10^3	1·29 × 10^3

TABLE III.

M/6000 Ferric Chloride (F) and Propionic Acid. $K=9$.

		Log I_o/I_t			x Calculated.
Wave-length	...	2961	2770	2445	
M/6000 F	...	·25	·35	·90	
M/5 acid	...	—	—	·25	
Mixture	...	·45	·50	—	·107 × 10^{-3}
E calc.	...	·45	·49		
M/10 acid	...	—	—	·15	
Mixture	...	·40	·45	1·35	·079 × 10^{-3}
E calc.	...	·40	·45	1·35	
M/20 acid	...	—	—	·10	
Mixture	...	·35	·40	1·20	·051 × 10^{-3}
E calc.	...	·35	·42	1·19	
M/50 acid	...	—	—	—	
Mixture	...	·30	·40	1·00	·025 × 10^{-3}
E calc.	...	·31	·38	·99	
M/100 acid	...	—	—	—	
Mixture	...	·25	·35	·95	·014 × 10^{-3}
E calc.	...	·28	·37	·95	
	E_M —	·94 × 10^3	·66 × 10^3	1·89 × 10^3	

In calculating the values of E, K has been assumed to be 9.

With M/3000 conc. of ferric chloride and varying concs. of propionic acid, observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=9$ and

λ ...	2961	2770
E_M ...	·93 × 10^3	·69 × 10^3

TABLE IV.

M/6000 Ferric Chloride (F) *and Oxalic Acid.* $K=240$.

		Log I_o'/I_t				α Calc.
Wave-length	...	3435	3364	3274	2961	
M/6000 F	...	·10	·15	·20	·25	
M/20 acid	...	—	—	·05	·30	
Mixture	...	·55	·60	·75	1·15	·154 × 10^{-3}
E calc.	...	·54	·59	·75	1·14	
M/40 acid	...	—	—	—	·15	
Mixture	...	·50	·55	·65	·95	·143 × 10^{-3}
E calc.	...	·51	·56	·66	·95	
M/100 acid	...	—	—	—	—	
Mixture	...	·45	·50	·60	·70	·118 × 10^{-3}
E calc.	...	·44	·49	·58	·70	
M/200 acid	...	—	—	—	—	
Mixture	...	·35	·40	·50	·60	·091 × 10^{-3}
E calc.	...	·36	·41	·49	·60	
M/400 acid	...	—	—	—	—	
Mixture	...	·30	·35	·40	·50	·062 × 10^{-3}
E calc	...	·28	·33	.40	·49	

In calculating the values of E, K has been assumed to be 240 in all the cases and E_M^{λ} given the following values for various wavelengths.

λ —	3435	3364	3274	2961
E_M —	1·45 × 10^3	1·45 × 10^3	1·62 × 10^3	1·93 × 10^3

With M/2000 conc. of ferric chloride and varying concs. of oxalic acid, observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=240$ and

λ —	3435	3364	3274	2961
E_M —	1·38 × 10^3	1·38 × 10^3	1·65 × 10^3	1·93 × 10^3

TABLE V.

M/6000 Ferric Chloride (F) and Malonic Acid. K=160.

		Log I_o/I_t			x Calculated.
Wave-length	...	2961	2600	2507	
M/6000 F	...	·25	·75	·85	
M/10 acid	...	—	—	·20	
Mixture	...	1·00	1·45	very large	·157 × 10^{-3}
E calc.	...	1·01	1·44		
M/20 acid	...	—	—	·10	
Mixture	...	·95	1·40	very large	·148 × 10^{-3}
E calc.	...	·96	1·40		
M/40 acid	...	—	—	·05	
Mixture	...	·90	1·35	1·45	·133 × 10^{-3}
E calc.	...	·89	1·33	1·44	
M/100 acid	...	—	—	—	
Mixture	...	·75	1·20	1·25	·102 × 10^{-3}
E calc.	...	·75	1·20	1·27	
M/200 acid	...	—	—	—	
Mixture	...	·60	1·10	1·15	·074 × 10^{-3}
E calc.	...	·61	1·07	1·15	
	E_M	$2·38 \times 10^3$	$2·20 \times 10^3$	$2·04 \times 10^3$	

In calculating the values of E, K has been assumed to be 160.

With M/3000 conc. of ferric chloride, and varying conc. of malonic acid, extinction coeffs. could be measured for higher wave-lengths and the observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=160$ and

λ	= 3574	2961
E_M	= $0·02 \times 10^3$	$2·38 \times 10^3$

TABLE VI.

M/6000 *Ferric Chloride (F) and Succinic Acid. K=110.*

		Log I_o/I_t		x Calculated.
Wave-length	...	2961	2770	
M/6000 F	...	·25	·35	
M/10 acid	...	—	—	
Mixture	...	·50	·55	·153 × 10^{-3}
E calc.	...	·50	·54	
M/20 acid	...	—	—	
Mixture	...	·50	·55	·141 × 10^{-3}
E calc.	...	·48	·53	

Wave-length	...	2961	2770	x Calc.
M/40 acid	...	—	—	
Mixture	...	·45	·50	·122 × 10^{-3}
E calc.	...	·45	·50	
M/100 acid	...	—	—	
Mixture	...	·40	45	·087 × 10^{-3}
E calc.	...	·39	·46	
M/200 acid	...	—	—	
Mixture	...	·35	·40	·059 × 10^{-3}
E calc.	...	·35	·42	
λ	–	2961	2770	
E_M	–	·84 × 10^3	·63 × 10^3	

In calculating the values of E, K has been assumed to be 110.

With M/3000 conc. of ferric chloride and varying conc. of succinic acid observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=110$ and

λ	–	2961	2770
E_M	–	·82 × 10^3	·61 × 10^3

TABLE VII.

M/6000 *Ferric Chloride* (F) *and Glycollic Acid.* $K=80$.

		Log I_o/I_t				x Calculated.
Wave-length	...	3435	2961	2722	2507	
M/6000 F	...	·10	·25	·50	·85	
M/5 acid	...	—	—	·30	·40	
Mixture	...	·45	·70	1·15	1·45	·143 × 10^{-3}
E calc.	...	·45	·69	1·15	1·46	
M/10 acid	...	—	—	·15	·20	
Mixture	...	·40	·65	·95	1·25	·125 × 10^{-3}
E calc.	...	·40	·64	·96	1·24	
M/20 acid	...	—	—	·05	·10	
Mixture	...	·35	·55	·80	1·10	·100 × 10^{-3}
E calc.	...	·35	·56	·79	1·10	
M/50 acid	...	—	—	—	—	
Mixture	...	·25	·45	·65	·95	·062 × 10^{-3}
E calc.	...	·25	·44	·65	·94	
M/100 acid	...	—	—	—	—	
Mixture	...	·20	·35	·60	·90	·038 × 10^{-3}
E calc.	...	·19	·37	·59	·91	

In calculatiug the values of E, K has been assumed to be 30 in all the cases and E_M^{λ} given the following values for various wave-lengths

λ	3435	2961	2722	2507
E_M	$1{\cdot}23\times10^3$	$1{\cdot}56\times10^3$	$1{\cdot}23\times10^3$	$\cdot75\times10^3$

With M/3000 conc. of ferric chioride and varying concs. of glycollic acid observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=30$ and

λ	3435	2961
E_M	$1{\cdot}21\times10^3$	$1{\cdot}56\times10^3$

TABLE VIII.

M/6000 Ferric Chloride (F) and Lactic Acid. $K=17$.

		Log I_0/I_t.				x Calc.
Wave-length		3364	2961	2722	2507	
M/6000 F	...	·15	·25	·50	·85	
M/acid	...	—	—	·30	·60	
Mixture	...	·55	·75	1·45	very large	$\cdot157\times10^{-3}$
E calc.	...	·53	·76	1·45	...	
M/5 acid	...	—	—	—	·15	
Mixture	...	·45	·65	1·05	1·45	$\cdot129\times17^{-3}$
E calc.	...	·46	·67	1·03	1·48	
M/10 acid	...	—	—	—	·10	
Mixture	...	·40	·60	·95	1·35	$\cdot105\times10^{-3}$
E calc.	...	·41	·59	·93	1·34	
M/20 acid	...	—	—	—	·05	
Mixture	...	·35	·50	·80	1·15	$\cdot076\times10^{-3}$
E calc.	...	·33	·50	·82	1·18	
M/50 acid	...	—	—	—	—	
Mixture	...	·25	·40	·65	1·00	$\cdot042\times10^{-3}$
E calc.	...	·25	·39	·67	1·01	

In calculating the values of E, K has been assumed to be 17 in all the cases and E_M^{λ} given the following values for various wave-lengths—

$\lambda=$	3364	2961	2722	2507
$E_M=$	$1{\cdot}20\times10^3$	$1{\cdot}63\times10^3$	$2{\cdot}07\times10^3$	$1{\cdot}86\times10^3$

With M/3000 conc. of ferric chloride and varying concs. of lactic acid, extinction coeffs. could be measured for higher wave-lengths,

and the observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=17$ and

λ =	3435	3364	2961
E_M =	$1\cdot03\times10^3$	$1\cdot17\times10^3$	$1\cdot59\times10^3$

TABLE IX.

M/6000 Ferric Chloride (F) and Tartaric Acid. K=40.

		Log I_0/I_t.				*x* Calc.
Wave-length		3435	2961	2722	2507	
M/6000 F	...	·10	·25	·50	·85	
M/2 acid	...	—	—	·30	1·00	
Mixture	...	·90	·60	1·30	very large	$\cdot159\times10^{-3}$
E calc.	...	·91	·61	1·30	...	
M/10 acid	...	—	—	·05	·20	
Mixture	...	·80	·55	·95	1·30	$\cdot133\times10^{-3}$
E calc.	...	·78	·55	·97	1·30	
M/20 acid	...	—	—	—	·10	
Mixture	...	·65	·50	·85	1·15	$\cdot11\times10^{-3}$
E calc.	...	·67	·50	·85	1·16	
M/40 acid	...	—	—	—	·05	
Mixture	...	·50	·45	·75	1·05	$\cdot083\times10^{-3}$
E calc.	...	·52	·44	·76	1·06	
M/100 acid	...	—	—	—	—	
Mixture	...	·35	·35	·65	·95	$\cdot047\times10^{-3}$
E calc.	...	·34	·35	·65	·94	

In calculating the values of E, K has been assumed to be 40 in all the cases and E_M^{λ} given the following values for various wave-lengths—

λ =	3435	2961	2722	2507
E_M =	$2\cdot55\times10^3$	$1\cdot12\times10^3$	$1\cdot59\times10^3$	$\cdot94\times10^3$

With M/3000 conc. of ferric chloride and varying conc. of tartaric acid observed values of extinction coeffs. for mixtures could be reproduced by assumiug $K=40$ and

λ =	3435	2961
E_M =	$2\cdot56\times10^3$	$1\cdot13\times10^3$

TABLE X.

M/6000 *Ferric Chloride (F) and Citric Acid.* $K=24$.

		Log I_0/I_t.				*x* Calc.
Wave-length		3274	2961	2770	2722	
M/6000 F	...	·20	·25	·35	·50	
M/3 acid	...	—	—	—	—	
Mixture	...	·40	·60	·80	1·00	$·148\times10^{-3}$
E calc.	...	·40	·59	·80	·98	
M/15 acid	...	—	—	—	—	
Mixture	..	·35	·50	·65	·85	$·102\times10^{-3}$
E calc.	...	·34	·48	·66	·83	
M/30 acid	...	—	—	—	—	
Mixture	...	·30	·40	·55	·75	$·074\times10^{-3}$
E calc.	...	·31	·42	·58	·74	
M/60 acid	...	—	—	—	—	
Mixture	...	·25	·35	·50	·65	$·047\times10^{-3}$
E calc.	...	·27	·36	·49	·65	
M/150 acid	...	—	—	—	—	
Mixture	...	·20	·30	·40	·55	$·023\times10^{-3}$
E calc.	...	·23	·30	·42	·58	

In calculating the values of E, K has been assumed to be 24 in all the cases and E_M^{λ} given the following values for various wave-lengths—

λ =	3274	2961	2770	2722
E_M =	$·69\times10^3$	$1·14\times10^3$	$1·53\times10^3$	$1·63\times10^3$

With M/3000 conc. of ferric chloride and varying concs. of citric acid, extinction coeffs. could be measured for higher wave-lengths and the observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=24$ and

λ =	3435	3364	3274	2961	2770
E_M =	$·49\times10^3$	$·49\times10^3$	$·67\times10^3$	$1·12\times10^3$	$1·60\times10^3$

TABLE XI.

M/6000 *Ferric Chloride* (*F*) *and Mandelic Acid.* $K=100$.

		Log I_0/I_1.				*x* Calc.
Wave-length		3435	2961	2770	2722	
M/6000 F	...	·1	·25	·35	·5	
M/10 acid	...	—	—	·4	...	
Mixture	...	·80	·70	1·35	...	$·151 \times 10^{-3}$
E calc.	...	·80	·68	1·36	...	
M/20 acid	...	—	—	·2	1·5	
Mixture	...	·75	·65	1·10	very large	$·139 \times 10^{-3}$
E calc.	...	·74	·65	1·11	...	
M/50 acid	...	—	—	·05	·6	
Mixture	...	·60	·55	·85	1·5	$·11 \times 10^{-3}$
E calc.	...	·61	·56	·85	1·5	
M/100 acid	...	—	—	—	·3	
Mixture	...	·50	·50	·70	1·1	$·083 \times 10^{-3}$
E calc.	...	·48	·49	·69	1·1	
M/200 acid	...	—	—	—	·15	
Mixture	...	·35	·40	·55	·85	$·055 \times 10^{-3}$
E calc.	...	·36	·41	·57	·85	

In calculating the values of E, K has been assumed to be 100 in all the cases and E_M^{λ} given the following values for various wave-lengths—

λ = 3455	2961	2770	2722
$E_M = 2·31 \times 10^3$	$1·42 \times 10^3$	$2·02 \times 10^3$	$1·80 \times 10^3$

With M/3000 conc. of ferric chloride and varying concs. of mandelic acid, extinction coeffs. could be measured for higher wave-lengths and the observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=100$ and

λ = 3435	2961	2770
$E_M = 2·25 \times 10^3$	$1·25 \times 10^3$	$2·03 \times 10^3$

Inferences.—The values of the dissociation constant of the intermediate complex formed of ferric salt and respective acids have always been correspondingly double those of uranyl salt complexes, or nearly so.

The values of molar extinction coefficients of the intermediate compound are also correspondingly greater.

Regularities observed between the values of K and the constitution of acids severally:

(1) The value of K diminishes as we go higher up in the series for each substitution of a (CH_2) group:

$$\frac{\text{Formic}}{\text{Acetic}} = \frac{16}{11} = 1{\cdot}45; \qquad \frac{\text{Acetic}}{\text{Propionic}} = \frac{11}{9} = 1{\cdot}22;$$

$$\frac{\text{Oxalic}}{\text{Malonic}} = \frac{240}{160} = 1{\cdot}5; \qquad \frac{\text{Malonic}}{\text{Succinic}} = \frac{160}{110} = 1{\cdot}45.$$

(2) The value of K increases as the hydrogen atom of a (CH_2) group is replaced by a (COOH) group.

$$\frac{\text{Oxalic}}{\text{Formic}} = \frac{240}{16} = 15{\cdot}0; \qquad \frac{\text{Malonic}}{\text{Acetic}} = \frac{160}{11} = 14{\cdot}5;$$

$$\frac{\text{Succinic}}{\text{Propionic}} = \frac{110}{9} = 12{\cdot}2.$$

(3) The replacement of a hydrogen atom in a (CH_2) group by an (OH) group increases the value of K.

$$\frac{\text{Glycollic}}{\text{Acetic}} = \frac{30}{11} = 2{\cdot}7; \qquad \frac{\text{Lactic}}{\text{Propionic}} = \frac{17}{9} = 1{\cdot}9.$$

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"After-effect" in certain Photochemical Reactions. Part II.

By B. K. Mukerji and N. R. Dhar.

In a previous paper (*J. Indian Chem. Soc.*, 1926, **2**, 227) we have shown that the phenomenon of "after-effect" is of common occurrence in photochemical reactions.

We have carried on further work in this line and have observed that the following photochemical reactions exhibit the phenomenon of after-effect: (*i*) ferrous sulphate and iodine; (*ii*) oxalic acid and iodine; (*iii*) sodium nitrite and iodine; (*iv*) the bleaching of dicyanin; (*v*) sodium malate and iodine; (*vi*) sodium formate and mercuric chloride; (*vii*) sodium lactate and iodine; (*viii*) decomposition of Fehling's solution in presence of ferric chloride; (*ix*) copper sulphate and ammonium oxalate in presence of ferric chloride; (*x*) decomposition of potassium mangani-oxalate.

Experimental.

In the present series of experiments, with a view to obtain a more marked effect, the reacting substances were in all cases first exposed to strong sunlight.

Hollow cubes made of transparent quartz were used for these experiments. One cube containing the reacting substance was exposed to light in a thermostat, another cube was placed in the dark at the same temperature. After exposure to light for a noted interval of time the vessel was removed to darkness and the reaction velocities were determined by the usual methods. The following experimental results were obtained:—

I. *Ferrous Sulphate and Iodine.*

$FeSO_4$—N/6·7; I_2—N/90; KI—N/19·86 and H_2SO_4—N/3. Temperature 21°.

Removed to darkness after 10 minutes' exposure to sunlight.

t (Mins.)	$(a-x)$ Thiosulphat in c.c.	$K_1 \times 1/2·3$ (Uni-mol.).
0	7·3	...
10	7·15	0·00090
55	6·95	0·000273*
135	6·65	0·000252
	Mean	0·000264

In the dark throughout.

t (Mins.)	$(a-x)$ Thiosulphate in c.c.	$K_1 \times 1/2·3$ (Uni-mol.).
0	7·3	...
35	7·15	0·000257
100	6·9	0·000245
220	6·45	0·000244
	Mean	0·000248

II. *Oxalic Acid and Iodine.*

Oxalic acid—N/5·192; I_2—N/113·6 in KI—N/29·4. Temperature 32°.

Removed to darkness after 26 minutes' exposure to sunlight.

t (mins).	$(a-x)$ Thiosulphate in c.c	$K_1 \times 1/2·3$ (Uni-mol).
0	4·6	...
26	3·45	0·00481
64	2·7	0·00280
80	2·55	0·00243
166	2·15	0·00228
	Mean	0·00250

In the dark throughout.

t (mins.)	$(a-x)$ Thiosulphate in c.c.	$K_1 \times 1/2·3$ (Uni-mol.)
0	4·6	...
23	4·05	0·00240
38	3·75	0·00234
53	3·5	0·00224
84	2·96	0·00228
	Mean	0·00232

III. *Sodium Nitrite and Iodine.*

$NaNO_2$—N/1·5; I_2—N/36·1 in KI—N/8·04 and CH_3COONa—N/6. Temperature 16°.

Exposed to sunlight for 34 minutes.

t (mins).	$(a-x)$ Thiosulphate in c.c.	$K_1 \times 1/2·3$ (Uni-mol.)
0	8·5	...
34	7·7	0·00126
64	7·55	0·000287
114	7·4	0·000216
184	7·15	0·000215
	Mean	0·000239

Entirely in the dark.

t (mins).	$(a-x)$ Thiosulphate in c.c.	$K_1 \times 1/2·3$ (Uni-mol.)
0	8·5	...
50	8·3	0·000206
110	8·05	0·000215
170	7·8	0·000219
240	7·55	0·000215
	Mean	0·000214

* For the calculation of this and the succeeding constants, zero-time was reckoned from the moment the light was cut off. This procedure was adopted in all the following reactions.

IV. *The Bleaching of Dicyanin.*

The rate of bleaching was followed by observing at noted intervals of time the extinction coefficient of the dye by means of a Hilger-Nutting spectro-photometer.

Dicyanin—M/15,500. Temperature 16°.

Zero error—0·69 on the density scale.

Thickness of the observation cell—0·5 cm. internally.

Exposed to sun-light for 10 minutes.				Entirely in the dark.			
t (mins).	Corrected reading on the density scale.	Extinction coefficient.	$K_1 \times \frac{1}{2 \cdot 3}$ (Uni-mol.)	t (mins.)	Corrected reading on the density scale.	Extinction coefficient.	$K_1 \times \frac{1}{2 \cdot 3}$ (Uni-mol.)
0	1·41	2·82	...	0	1·41	2·82	...
10	0·59	1·18	0·0378	90	0·86	1·72	0·00239
63	0·41	0·82	0·00293	140	0·66	1·32	0·00235
145	0·26	0·052	0·00245	230	0·40	0·80	0·00238
250	0·16	0·032	0·00236	270	0·32	0·64	0·00238
		Mean	0·00260			Mean	0·00238

V. *Sodium Malate and Iodine.*

Sodium malate—N/6·78; I_2—N/111·6 in KI—N/33·7. Temperature 32°.

Removed to darkness after 16 minutes' exposure to light.			In the dark throughout.		
t (mins).	$(a-x)$ Thiosulphate in c.c.	$K_1 \times \frac{1}{2 \cdot 3}$ (Uni-mol.)	t (mins).	$(a-x)$ thio in c.c.	$K_1 \times \frac{1}{2 \cdot 3}$ (Uni-mol.)
0	4·95	...	0	4·95	...
16	4·2	0·00446	25	4·45	0·00185
35	3·8	0·00228	33	4·3	0·00185
55	3·5	0·00203	49	4·0	0·00189
86	3·1	0·00188	75	3·6	0·00184
124	2·65	0·00185	108	3·1	0·00188
	Mean	0·00201		Mean	0·00186

VI. *Sodium Formate and Mercuric Chloride.*

CHOONa—0·954 N; $HgCl_2$—N/15 and CH_3COONa—0·2813 gm. in 20 c.c. of the reacting mixture. Temperature 32°.

Removed to darkness after 20 minutes' exposure to light.

t (mins).	$(a-x)$ KI in c.c.	$K_1 \times \frac{1}{2\cdot1}$ (Uni-mol.)
0	5·78	...
20	4·46	0·00563
33	4·04	0·00330
48	3·67	0·00302
68	3·15	0·00315
	Mean	0·00316

In the darkness throughout.

t (mins).	$(a-x)$ KI in c.c.	$K_1 \times \frac{1}{2\cdot3}$ (Uni-mol.)
0	5·78	...
7	5·5	0·00307
22	4·95	0·00306
35	4·47	0·00319
52	3·96	0·00316
	Mean	0·00312

VII. *Sodium Lactate and Iodine.*

Sodium lactate—N/9·7; I_2—N/112·85 in KI—N/20·72. Temperature 32°.

Exposed to light for 25 minutes.

t (mins.)	$(a-x)$ thio in c.c.	$K_1 \times \frac{1}{2\cdot3}$ (uni-mol.)
0	1·75	—
25	1·1	0·00806
38	0·95	0·00490
60	0·8	0·00395
85	0·65	0·00381
	Mean	0·00422

In the dark all along.

t (mins.)	$(a-x)$ thio in c.c.	$K_1 \times \frac{1}{2\cdot3}$ (uni-molr.)
0	1·75	—
14	1·55	0·00376
30	1·35	0·00376
53	1·10	0·00380
70	0·95	0·00379
	Mean	0·00378

VIII. *Decomposition of Fehling's Solution in Presence of Ferric Chloride.*

No appreciable after-effect was observed in this reaction using a 500 c.p. pointo-lite lamp. This experiment was now repeated in bright sunlight and an after-effect was observed.

To 50 c.c. Fehling's solution, 0·5 c.c. dilute ferric chloride solution was added and the mixture divided into two portions. One portion was exposed to strong sunlight and another was kept in the dark. After 1½ hours' exposure to sunlight a precipitate was observed in the first case while the other remained unchanged. Now, the solution exposed to sunlight was filtered through double filter paper and the filtrate removed to darkness. In this filtrate a deposit was noticeable after 1½ hours whereas the solution kept all along in the dark did not show any precipitate whatsoever.

IX. *Copper Sulphate and Ammonium Oxalate in Presence of Ferric Chloride.*

A mixture of M/2—$CuSO_4$, M/21 $(NH_4)_2C_2O_4$ and a small quantity of $FeCl_3$ was made up. This was divided into two portions. One kept in the dark while the other exposed to strong sunlight. The portion exposed to light showed a red deposit in a fairly large quantity after 20 minutes. This was now carefully filtered and the filtrate removed to darkness. A deposit appeared in this filtrate after 15 minutes while in the case of the mixture all along in the dark no deposit could be noticed.

X. *The Decomposition of Potassium-mangani-oxalate.*

This compound was prepared by the method described by Christiansen (*Z. anorg. Chem.*, 1911, **27**, 325).

Exposed to light for 2 minutes.			In the dark throughout.		
t (mins.)	$Na_2S_2O_3$ in c.c.	$K_1 \times \frac{1}{2\cdot3}$ (uni-molr.)	t (mins.)	$Na_2S_2O_3$ in c.c.	$K_1 \times \frac{1}{2.3}$ (uni-molr.)
0	0·8	—	0	0·8	—
2	0·6	0·0625	4·5	0·75	0·00622
8	0·4	0.0294	14·5	0·65	0·00622
20	0·35	0·0130	26	0·55	0·00626
65	0·25	0·00603	50	0·4	0·00602
	Mean	0·0161		Mean	0·00618

It was observed by Stark (*Ann. Phys.*, 1904, **14**, 520), Lord Rayleigh (*Proc. Roy. Soc.*, 1914, **90A**, 364 ; **91A**, 92; 1925, **108**, 262) and others that a stream of mercury vapour allowed to distil away from the arc or glow discharge in vacua remains luminous. Recently Asterblum (*Z. Physik*, 1927, **43**, 427) has shown that the duration of after-glow of mercury decreases in intensity logarithmically with time. This persistence of the glow in mercury and the phenomenon of after-effect as observed in photochemical reactions appear to be identical.

Wood (*Proc. Roy. Soc.*, 1921, **99**, 362) has come to the conclusion that though the normal life-period of activated atoms and molecules

is of the order 10^{-8} seconds, in some cases the life-period can be considerably prolonged and in several cases it comes out to be of the order 10^{-4}.

We are also of the opinion that the life-period of the activated molecules in photochemical reactions taking place in solution is considerably prolonged. The gradual vanishing of the influence of the activated molecules just after removal of the reacting system from light to darkness is evident by a concomitant decrease in the veclocity of the reaction till it has the same value as that obtained in the reaction taking place all along in the dark. Recently Eggert and his coworkers (*Z. Physik*, 1925, **26**, 865) have stated that excited bromine molecules have a relatively long life-period and is possibly of the order of 10^{-5} sec. We are of the opinion that the life-period of the activated molecules in the photochemical reaction taking place in solution is considerably prolonged and the slow reversion of the activated molecules into the inactive state is the main cause of the phenomenon of after-effect.

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Effect of Electrolytes on the Distribution of Acetic Acid between Benzene and Water.

By Ramprosad Mittra.

It is now more or less generally accepted that the Milner-Ghosh-Debye theory of strong electrolytes gives a satisfactory representation of the facts at high dilutions up to a concentration of ·01N. Above that concentration individual effects appear which cannot be accounted for by the Debye equations. Thus Scatchard and Harned in their attempt to prove the Debye equations have been led to attribute a negative diameter to atoms. Similarly a critical examination of Brönsted's data shows, as has been pointed out by Brönsted himself, that with unsymmetric electrolytes the Debye equations break down even at high dilutions. The Debye equations postulate that the free energy of dilution of electrolytes consists entirely of the work against electrical forces and do not take cognizance of any change in the state of hydration of the ions (*cf.* Nernst).

Further a consideration of the difficulties in the way of the Debye equations has led Bjerrum (*Svensk. Kem. Tidskr.*, 1926, **38**, 2) one of the originators of the hypothesis of complete dissociation to modify the fundamental postulate of this hypothesis by introducing the concept of ion-association which is obviously a formal confession of the failure of the hypothesis of complete dissociation in its original form.

It appears to the writer that before a complete theory of electrolytic dissociation can be established more exhaustive experimental investigations require to be undertaken with a view to elucidate specific differences between the properties of individual ions such as are not accounted for by the Debye equations. We have already indications of such differences even at moderate dilutions and for the simpler inorganic ions.

Subject Matter of Present Investigation.

In the present paper the influence of the common inorganic electrolytes, as for example potassium chloride, sodium chloride,

barium chloride, potassium nitrate, potassium sulphate, lithium chloride, sodium oxalate, lithium sulphate and sodium sulphate on the partition of acetic acid between benzene and water has been studied with a view to examine specific differences between the ions and the limiting concentrations above which such differences appear. The writer would refer to the earlier work on this subject of Dawson (*Zeit. physikal. Chem.*, 1906, **56**, 605), of Schreiner (*Zeit. anorg. Chem.*, 1921, **115**, 181) and of Cavanagh (*Proc. Roy. Soc.*, 1924, A **106**, 243).

The work of McBain and Kam (*J. Chem. Soc.*, 1919, **115**, 1332) on the effect of neutral salts on the partial vapour pressure of acetic acid over its aqueous solutions is most interesting in connection with the present work. They concluded that the increased hydrogen ion concentration on the addition of neutral salts deduced from electromotive force measurements of such solutions are to be referred to increased activity of the ions and not to an increase in dissociation. It is possible to extend the studies of Brönsted on the solubility of salts from a study of the effect of neutral salts on the partial pressure of acetic acid in this system and from a study of similar systems. Measurement of the partition ratio offers an easier experimental procedure than the measurement of vapour pressure. In the present case however it is obvious that the concentration of acetic acid in the benzene phase does not give as reliable a measure of the activity of acetic acid molecules in the solution as is given by its partial pressure in the vapour phase for we are dealing with a solution of acetic acid in aqueous benzene and not in pure benzene. The proportions of water in the benzene phase varies with the activity of water in the aqueous phase which is determined by the concentration and nature of the dissolved electrolyte. On account of the low solubility of water in benzene one may neglect this factor if an interpretation of the results is restricted to a qualitative discussion of the relative effects of different ions under comparable conditions on the activity of acetic acid. Comparison with the stricter procedure of McBain and Kam will give us also the necessary information about the effect of this disturbing factor.* We find that our results are in general agreement with those of McBain and Kam. As we shall see later the present method has also the advantage of being sensitive to slight variations in activity of acetic acid on the addition of salts.

* An independent investigation of the partial pressure of acetic acid over its benzene solution containing varying amounts of water will enable us to quantitatively measure the activity of acetic acid in such solutions.

Experimental.

The distribution of acetic acid between benzene and water was obtained with and without the addition of different concentrations of salts; two concentrations of acid were used, one near about 0·5N and the other near about 0·35N; the concentration of the neutral salts was varied from 0·01 to 3 or 4N. Pure chemicals tested before use were always employed. The thermostat was maintained at 35°.

In all cases except otherwise mentioned 50 c.c. of the solution made up by mixing 25 c.c. of the acid of known strength and 25 c.c. of the standard salt solution were introduced together with 50 c.c. of extra pure crystallisable benzene into thoroughly cleansed and dried 100 c.c. jena glass bottles; the bottles with their contents were thoroughly shaken in a machine for about fifteen minutes; they were then tied on to a rotating axle inside the thermostat to secure equilibrium distribution between the two phases at the required temperature, the equilibrium being attained in less than three hours as found by titration after definite intervals. The bottles were then left in the thermostat with the necks just above the water; measured volumes from the benzene and aqueous phase were taken and titrated against air free standardised baryta solution. Results are given in the following tables.

The five tables under Series I give respectively the results with sodium chloride, potassium chloride, potassium nitrate, barium chloride and potassium sulphate. The first column gives the molar concentration of the salt used; the second gives the 'ionic strength'; the third gives the concentration of acid in the benzene phase in terms of normality; the fourth gives the concentration in the aqueous phase; the fifth column gives the ratio (R_1) of the concentrations of the acid in the benzene and in the aqueous phase with the addition of the salt ; the sixth gives the same ratio (R_2) obtained without the addition of the salt ; the last column gives the percentage increase of the first ratio over the second ratio R_2, *i.e.*, 100 $(R_1—R_2)/R_2$, this quantity magnifies the relative effect of the added salt and its concentration on the distribution of acetic acid between the two phases (*cf.* McBain and Kam, *loc. cit.*)

Electromotive force measurements were also carried out to form an idea of the change in the activity of the hydrogen ion on the addition of neutral salts. The results are given in the six tables under Series II and III ; with one portion of the solution the electro-

motive force was determined and another portion of the solution was used for determining the distribution ratios by titration. The activity of the hydrogen ion as measured in terms of the hydrogen ion concentration (p_H) using the Nernst equation is given in the last column. The hydrogen ion activity therefore refers to the original solution before partition ; the actual values of the electromotive force for the same solutions are given in the appendix. The cell studied was of the type :

$Pt(H_2)$/HAC (salt solution)/sat. KCl/HgCl/Hg (*N*.KCl), the reference electrode being the normal calomel electrode. The potentiometer used was the "K" type instrument of Leeds and Northrup & Co. The thermostat was maintained at 35° ± ·02° ; extra pure arsenic-free zinc and extra pure acid were used for preparing the hydrogen; under the conditions results reproducible within ± ·05 millivolt were obtained in the case of solutions containing higher concentration of the salts ; with very dilute solutions of the salts results reproducible to within ± 0·1 millivolt were always obtained. The liquid junction potential has been taken to be zero. Equilibrium in all cases was established in less than four hours.

In Series II and III the first column gives the concentration of the salt; the second gives the "ionic strength" ; the third gives the concentration of the acid in terms of normality in the benzene phase ; the fourth that in the aqueous phase ; the fifth gives the ratio $R_1 = C_B/C_W$, when salt is present ; the sixth gives R_2 the same ratio without addition of salt ; the seventh gives the quantity $100\,(R_1 - R_2)/R_2$; the last gives the p_H value of the original solution before partition. In the fourth and fifth series results are given in the same way with the difference that the electromotive force measurements were made in the solutions after shaking with benzene and determining the distribution ratio by titration ; thus the E.M.F. measurements were carried out in solutions in equilibrium with the benzene phase.

Series I.

(*i*) *Conc. of the acid*—0·494 N ;
Salt added—*Sodium chloride.*

Conc. of salt.	Ionic strength (μ)	C_B	C_W	R_1	R_2	$100.\frac{R_1-R_2}{R_2}$
·5M	·994	·0128	·481	·0265	·0228	15·9
·25M	·744	·0119	·482	·0247	,,	8·34
·1M	·594	·01176	·484	·0243	,,	6·2
·05M	·544	·0116	·483	·0241	,,	5·46

(ii) Conc. of the acid—·497N ;
Salt added—Potassium chloride.

Conc. of salt.	Ionic strength (μ)	C_B	C_W	R_1	R_2	$100.\frac{R_1-R_2}{R_2}$
·5M	·997	·0126	·484	·0262	·0228	14·4
·25M	·747	·0120	·485	·0247	,,	7·9
·1M	·597	·0113	·486	·0233	,,	1·8

(iii) Conc. of the acid—0·493N ;
Salt added—potassium nitrate.

5M	·993	·01135	·481	·0238	·02275	4·05
·25M	·743	·011	·483	·0235	,,	2·7
·1M	·593	·011	·483	·0235	,,	2·7
·05M	·543	·0107	·484	·0231	,,	1·17

(iv) Conc. of the acid—·497N ;
Salt added—Barium chloride.

·25M	1·247	·01332	·485	·02745	·0228	20·3
·125M	·872	·0123	·487	·0252	,,	10·8
·05M	·647	·0117	·486	·0241	,,	5·7
·025M	·572	·01165	·486	·0239	,,	5

(v) Conc. of the acid—0·496N ;
Salt added—Potassium sulphate.

·25M	1·246	·01245	·482	·0258	·0228	13·1
·125M	·871	·0118	·484	·0246	,,	8·06
·05M	·646	·01145	·485	·0236	,,	3·6

Series II.

(vi) Conc. of the acid—·5065N ;
Salt added—Potassium chloride.

Conc. of salt.	Ionic strength (μ)	C_B	C_W	R_1	R_2	$100\frac{R_2-R_3}{R_3}$	p_H
·5M	1·006	·01197	·490	·0244	·0211	15·6	2·356
·25M	·756	·0105	·492	·0214	,,	1·2	2·374
·05M	·556	·0105	·495	·0212	,,	·8	2·409
No salt	...	·0105	·500	...	,,	...	2·411

(vii) Conc. of the acid—0·5065N ;
Salt added—Sodium chloride.

·5M	1·006	·0121	·4906	·0246	·0211	16·9	2·302
25M	·756	·01124	·4911	·0229	,,	8·5	2·335
·1M	·606	·01117	·4922	·0227	,,	7·6	2·359
·05M	·556	·0111	·4924	·02255	,,	6·9	2·374

Series III.

(viii) Conc. of the acid—0·362N;
Salt added—Barium chloride.

Conc. of salt.	"μ" ionic strength.	C_B	C_W	R_1	R_2	$100.\frac{R_1-R_2}{R_2}$	p_H
·25M	1·16	·0075	·3536	·0213	·01876	13·4	2·267
·125M	·73	·0071	·355	·0200	,,	6·6	2·334
·05M	·51	·0071	·358	·01984	,,	5·7	2·367
·025M	·44	·0069	·358	·0194	,,	3·4	...
No salt	...	·0063	·355	...	,,	...	2·415

(ix) Salt added—Potassium nitrate.

·5M	·86	·0069	·357	·0195	·01876	3·9	2·402
·1M	·46	·0067	·358	·018765	·01876	·05	2·307

(x) Salt added—Sodium oxalate.

·125M	...	·369	·358	·0192	·01876	2·3	3·495
·05M	...	·368	·357	·0184	,,	—1	3·474
·025M	...	·368	·358	·0183	...	—2	3·088

(xi) Salt added—Potassium sulphate.

·25M	1·11	·00697	·355	·0196	·0116	4·4	2·809
·125M	·737	·0065	·356	·0184	·01876	—1	2·727
·05M	·512	·0064	·357	·0178	·01876	—5·1	2·651
·025M	·437	...	...	...	...	...	2·622

Series IV.

(xii) Conc. of the acid—·35 N;
Salt added—Potassium chloride.

3 M	3·35	·00908	·341	·0264	0·18759	40·7	2·276
2·5M	2·55	·00859	·342	·025	,,	34	2·295
2M	2·35	·00823	·3437	·0240	,,	28	2·307
1·5M	1·85	·00804	·3429	·0234	,,	24·7	2·316
1M	1·35	·00726	·3437	·02112	,,	12·5	2·331
·067M	·417	·00 65	·3427	·0194	,,	3·4	2·387
No salt	...	·0064	·345	...	,,	...	2·415

(*xiii*) *Salt added—Sodium chloride.*

Conc. of salt.	'μ' Ionic strength.	C_B	C_W	R_1	R_2	$100.\frac{R_1-R_2}{R_2}$	p_H
4M	4·35	·0151	·335	·04057	·018759	140·2	1·904
3·5M	3·85	·0137	·336	·04077	,,	117·3	1·954
3M	3·35	·0125	·337	·0371	,,	97·8	2·013
2·5M	2·85	·0125	·337	·0371	,,	97·8	2·021
2M	2·35	·01022	·339	·0301	,,	60·6	2·123
1·5M	1·85	·00901	·341	·0264	,,	41	2·17
1M	1·35	·00847	·334	·0253	,,	34·8	2·238
·2M	·55	·00671	·342	·0196	,,	4·4	2·344
·067M	·417	·00659	·344	·0192	,,	2·3	2·364
·02M	·37	·00651	·344	·0189	,,	·7	2·386

(*xiv*) *Salt added—Barium chloride.*

1·25M	4·1	·01029	·3397	·03033	·018759	61·6	1·95
1M	3·35	·00919	·340	·0270	,,	44·4	2·019
·75M	2·85	·00865	·341	·0254	,,	35·4	2·287
·5M	1·85	·00786	·342	·0231	,,	23·1	2·78
·1M	·65	·00677	·338	·0200	,,	6·6	2·325
No salt	...	·00640	·345	...	,,	...	2·415

SERIES V.

(*xv*) *Conc. of acid*—·5001N;
Salt added—Potassium nitrate.

·5M	2·0	·01077	·485	·0222	·02057	7·9	2·257
1M	1·5	·01065	·4855	·0219	,,	6·4	2·289
·2M	·7	01065	·4856	·0219	,,	6·4	2·331
·036M	·536	·01059	·4855	·0218	,,	5·9	2·331
·024M	·524	·01059	·4855	·0218	,,	5·9	2·336
·012M	·512	·01059	·4855	·0218	...	5·9	...
No salt	...	·01053	·4868	...	...	...	...

(*xvi*) *Salt added—Sodium sulphate.*

·255M	1·25	·0118	·485	·0243	·02057	18·1	2·334
·204M	1·11	·0113	·4855	·0234	,,	13·7	2·686
·153M	·96	·0119	·48510	·02307	,,	12·1	2·597
·102M	·80	·0109	·4855	·0225	,,	9·3	2·599
·051M	·68	·01065	·4858	·02192	,,	6·5	2·438
·00408M	·512	·01059	·4863	·0217	,,	5·4	2·364
·00204M	·50	·01046	·4865	·0215	,,	...	2·223

(*xvii*) *Salt added—Lithium chloride.*

2.33M	2·83	·0221	·456	·0464	·02057	125·5	1·829
1·863M	2·33	·01936	·477	·0405	,,	96·8	1·911
1·397M	1·89	·0167	·481	·0347	,,	68·6	1·997
·931M	·59	·0105	·484	·02188	,,	6·3	2·173

(*xviii*) *Salt added—Lithium sulphate.*

Conc. of salt.	'μ' Ionic strength.	C_B	C_W	R_1	R_2	$100.\frac{R_1-R_2}{R_2}$	P_B
·601M	2·90	·01736	·477	·0364	·02057	76·9	2·384
·641M	2·42	·0153	·481	·03177	,,	54·4	2·279
·481M	1·94	·0137	·482	·02867	,,	39·3	2·228
·320M	1·46	·0121	·483	·02508	,,	21·9	...
·160M	·980	·01097	·484	·02267	,,	10·2	2·018

Discussion.

As stated in the introduction the results permit only qualitative discussion as to the relative effects of neutral salts at different concentrations on tl e acetic acid molecules. Colateral measurements could not possibly be undertaken within the time at our disposal. We therefore restrict ourselves to point out the main features of the results.

In the case of all electrolytes excepting potassium sulphate and sodium oxalate the added salt produces increase in activity the magnitude of which increases with increase in concentration. We have three sets of measurements with potassium sulphate Tables No. 5, 11 and 15; the latter two tables deal with a lower concentration of acid than is the case with the first one. It appears that the concentration of the acid used has some effect for at the higher concentration of the acid (*vide* Table 5) the effect is positive at a concentration of ·1N and there is a decidedly greater activation. On a close examination of the data it will appear that on account of the low concentration in the benzene layer the relative value of the quantity $100(R_1-R_2)/R_2$ will be magnified by small experimental errors. At low concentration of the added salts where the change in the activity is small, variations in the above quantity are to be expected from the probable errors of measurements and unless the relative variation is marked it is not possible to draw any definite conclusion. It should be stated here that the above mentioned quantity has no physical significance except that it gives an idea of the extent of activation. Even taking these facts into consideration it is obvious that potassium sulphate behaves in a manner different from the other electrolytes as also from sodium sulphate and lithium sulphate.

McBain and Kam (*loc. cit.*) observed a slight negative effect of sodium sulphate below a concentration of 0·32N of the salt; they however used much lower concentration of the acid between 0·22N and 0·29N. As we have seen the concentration of the acid has also an

influence. Taking our observations in conjunction with those of McBain and Kam it appears that—

(*a*) The negative activation is the greatest for potassium sulphate and decreases in the order : potassium sulphate > sodium sulphate > lithium sulphate.

(*b*) That at sufficiently low concentrations of the acid and of these salts this effect can be expected for all the sulphates.

It is likely that further investigation may establish that the negative activation should be ascribed to the sulphate ion and that potassium, sodium and lithium, all produce a positive activation which increases in the order given above, *viz.* lithium > sodium > potassium.

The sulphates also show another characteristic difference, *viz.*, that the activity of the hydrogen ion decreases with increasing concentration of the salt. We are here again dealing with specific influences. We have to take into consideration the formation of HSO_4 ion in explaining this effect. This appears more plausible in view of the fact that sodium oxalate also shows similar effect whereas barium chloride increases the activity of the hydrogen ion at all concentrations though the sulphates and barium chloride are electrolytes of the same type. Potassium nitrate also shows a characteristic behaviour. The activation of the acetic acid molecule is slight and also it has little effect on the activity of the hydrogen ion. With the nitrate also the concentration of the acid seems to have an effect. At lower concentration positive activation is diminished. Also change in activation with the concentration of the salt is small.

Considering the chlorides we again find that the activation is in the order Li > Na > K. Barium chloride at the same time ionic strength has a decidedly smaller effect than either lithium or sodium chloride and has more or less the same effect as potassium chloride. The order Li > Na > K is the same as the order of increasing atomic diameters. Dawson (*loc. cit.*) observed for ammonia and iodine the following order of decreasing activating capacity of anions: SO_4 > Oxalate > Cl' > NO'_3 > Br' > I'.

The variation in activation of acetic acid molecules with concentration is different for different salts. Here we find, specific differences are not appreciable at very low concentration. To sum up we find that—

(*i*) The chlorides increase the activity of the hydrogen ion within the range of our investigation as also of acetic acid molecules.

(*ii*) The ionic strength of the electrolyte is not the only factor but that the sign of the charge of the ion has also to be taken into consideration.

(*iii*) The activating effect of the electrolyte on acetic acid molecule does not always run parallel with its effect on the hydrogen ion.

(*iv*) In the case of the sulphates we are dealing with opposing effects of the cation and the anion on the activation of acetic acid molecules. Such effects are already known. Thus Thomas and Baldwin (*J. Chem. Soc.*, 1919, **115**, 1981) have observed that the sulphates behave differently from the chlorides and that at low concentrations the sulphates diminish the activity of the hydrogen ion in solutions of hydrochloric and sulphuric acids but as the concentration increases the activity begins to increase after a certain concentration. There is a characteristic influence of the cation, the magnesium ion showing the greatest increase in activity at the higher concentrations. They also observed that the relative effect of a neutral salt on the activity of hydrogen ion depends on the concentration of the acid (sulphuric).

The question arises whether the effect of the electrolyte on neutral acetic acid molecules is simply made up of its effect on the activities of the hydrogen ion and acetanion or that the activity coefficient of the neutral acetic acid molecules also changes in the presence of neutral electrolytes. The colateral investigations we have referred to are likely to give valuable information on the point. If, as we observe, the sign of the charge and the valency of the ions of neutral electrolytes (apart from their specific influences depending on their diameter or their structure) has an effect it stands to reason that they will have an effect on the anion of the acid; the magnitudes of the two effects will however be different and vary in a different manner with changes in the external conditions. That such an effect is present appears from the fact that though the sulphates decrease the activity of the hydrogen ion (it is specially marked at higher concentrations of the salt) they increase considerably the activity of the acetic acid molecules. It is likely that this in part is due to the activation of the anion but as just stated we are not in a position to say anything definitely so long as we have no knowledge of the effect of electrolytes on the activity of neutral acetic acid molecules.

In conclusion we shall hazard the opinion that the so called agreement with the Debye equations is more or less fortuitous as

the investigations quoted in their support have been too limited in their scope and that factors like existence of undissociated molecules in aqueous solution or the ion association of Bjerram and the hydration of ions are not negligible even at low concentrations of of the order of 0·01N.

Since this work was completed a paper by Knight and Hinshelwood (*J. Chem. Soc.*, 1927, **131**, 466) has appeard. The authors from measurements of distribution of HCl between water and benzene conclude that there is definite evidence for the existence of undissociated molecules in the water phase at higher concentration.

In a recent paper Sugden (*J. Chem. Soc.*, 1926, **129**, 174) has given the distribution coefficient of acetic acid between amyl alcohol and aqueous solutions of salts from which he has calculated the extent of hydration. His results however cannot be compared with those of ours so that detailed reference to his paper is unnecessary.

I would express my best thanks to Prof. J. N. Mukherjee, D.Sc., for suggesting this subject to me and for his guidance and help.

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A new Method of Preparing Organo-mercury Compounds of Phenols, Phenol-ethers and aromatic Amines.

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The preparation of aromatic compounds of mercury was first extensively undertaken by Dimroth (*Ber.*, 1898, **31**, 2154 *et seq.*) Pesci (*Gazzetta*, 1898, **28**, *ii*, 436 *et seq.*) and several others. The introduction of mercury into various organic compounds has hitherto almost uniformly been effected by heating them with mercuric acetate. In the case of mercuri-chlorides of aromatic organic compounds the acetate is decomposed by means of sodium chloride. Dimroth (*Ber.*, 1899, **32**, 758) has shown that besides the acetate such mercuric salts as the sulphate and the nitrate, which are hydrolysed by water, are capable of acting on aromatic organic compounds: but mercuric chloride has been found to have very little action, if any, on aromatic compounds.

In this paper it has been shown that mercury derivatives of aromatic compounds can be prepared mostly in the cold by the action of mercuric chloride along with sodium bicarbonate on these compounds. Neogi and Neogi (*J. Chem. Soc.*, 1927, **131**, 30) have recently shown that a distinct period of induction exists when mercuric chloride and sodium bicarbonate are allowed to act before oxychlorides of mercury are precipitated. They have further shown that, amongst other substances, glycerol has the property of very largely increasing the period of induction in the interaction of mercuric chloride and sodium bicarbonate. Advantage has been taken of this phenomenon in this paper to prepare organic mercury compounds of aromatic phenols, phenol-ethers and amines by adding the organic compound to the mixture of sodium bicarbonate and mercuric chloride in the presence of glycerol. This is a very interesting phenomenon, as it shows the possibility of formation of compounds with new reactants added during the period of induction before the main reaction finds time to be completed. As the formation of oxychloride of mercury requires time which might be indefinitely increased by the presence of glycerol, the organic compounds introduced in the mixture combine with the reactants and form new

compounds. The organic substance and mercuric chloride solution are mixed together, glycerol is then added followed by the sodium bicarbonate solution. Sometime the order of the addition is reversed. In the case of substances not soluble in water alcoholic solutions are taken. This method might be made a general process of preparing organo-mercury compounds.

The reactions that take place in the case of phenols and phenol-ethers may be represented by the following equations:

$$C_6H_4(OH)_2 + HgCl_2 + NaHCO_3 = C_6H_4(OH)(OHgCl) + NaCl + CO_2 + H_2O$$

$$C_6H_4(OH)(OHgCl) + HgCl_2 + NaHCO_3 = C_6H_4(OHgCl)_2 + NaCl + CO_2 + H_2O$$

In the case of catechol, quinol, resorcinol, phloroglucinol, guaiacol and orcinol, mono- and di-oxydimercuri-chlorides of the phenols and phenol-ethers are formed as the case may be. In the case of phenol however *o*- and *p*-hydroxyphenylene mercuri-chlorides are formed according to the equation:—

$$C_6H_5(OH) + HgCl_2 + NaHCO_3 = C_6H_4(OH)(HgCl)(o\text{- and } p\text{-}) + NaCl + CO_2 + H_2O$$

So far as amines are concerned it is to be remembered that mercuric chloride gives crystalline additive derivatives of the type $(C_6H_5NH_2)_2HgCl_2$ (Forster, *Annalen*, 1875, **175**, 30). In order to prepare mercury derivatives by this method, sodium bicarbonate solution was added first to aqueous or alcoholic solutions of the amines, and then the mercuric chloride solution was added. In the case of the amines the addition of glycerol is not necessary owing to the prior formation of the additive derivatives. In the case of primary and secondary aromatic amines the following equations represent the reactions that take place:—

$$PhNH_2 + HgCl_2 + NaHCO_3 = PhNH.HgCl + NaCl + CO_2 + H_2O$$

$$PhNH.CH_3 + HgCl_2 + NaHCO_3 = PhNCH_3.HgCl + NaCl + CO_2 + H_2O$$

In the case of tertiary amines the HgCl radical replaces a hydrogen in the benzene nucleus or forms a complex molecule.

As regards the question whether the radical HgCl enters the nucleus or forms oxy-mercurichlorides in the case of phenols and phenol-ethers the following experimental evidences point to the formation of oxy-mercuri-chlorides excepting in the case of phenol :—

1. These mercury compounds except that of phenol are not soluble in caustic soda and hence do not contain phenolic hydroxyl groups.

2. These compounds are generally decomposed by caustic soda into mercuric chloride and the sodium derivatives of original phenols.

3. These oxy-mercuri-chlorides are new compounds which do not correspond in properties to mercuri-chloride derivatives of phenols in which the radical HgCl has entered the nucleus.

In the case of the amino-compounds the HgCl radical replaces the hydrogen in the amino-group and not in the nucleus as the usual evidences of the presence of amino-groups, such as the formation of azo-dyes in the case of primary amines, are wanting in the case of these compounds. As regards tertiary amines, owing to the absence of hydrogen in the amino-group, the HgCl radical replaces hydrogen in the nucleus.

These oxy-mercuri-chlorides are generally white or light yellow in colour. The catechol compound is green and the guaiacol compound is deep yellow. The amino-compounds are generally yellow in colour. They are all insoluble in water and in most organic solvents. They are mostly soluble in hot mineral acids but insoluble in caustic soda which decomposes them. The mercury compounds prepared by this new method from catechol, orcinol, resorcinol, phloroglucinol, guaiacol, and quinol are new compounds. The yield is quite good.

As regards analytical results the mercury was estimated by two methods: (1) Marsh and Lye's method (*Analyst*, 1917, **42**, 84), and (2) Francois' method (*Compt. rend*, 1918, **166**, 950, and *Bull. Soc. Chim.*, 1920, [IV], **27**, 568). As regards the former method our experience is that it is best to increase the proportion of calcium sulphate to four or five times instead of twice the weight of the substance to be analysed in order to prevent the distillation of tarry matter. Even with this precaution the free mercury obtained, specially in the case of amino-compounds, was found to be contaminated with small quantities of brown organic matter. In those cases therefore the mercury was washed with ether before drying and weighing. As regards Francois' method our experience is that it gives good results though it takes nearly four days to get the final weight of the mercury. The advantage of Francois' method however lies in the

fact that several estimations can be started in one day and the result obtained simultaneously at the end of four days. Both these methods of estimating mercury in organic compounds are to be recommended in preference to the usual method of estimating it as HgS after the destruction of organic matter in a sealed tube in a Carius' furnace.

The chlorine was estimated by Piria and Schiff's method which works well in the case of these compounds.

Experimental.

o- *and* p-*Hydroxyphenylene mercurichloride*, $C_6H_4\begin{cases}(OH)(1)\\HgCl(2),(4)\end{cases}$

Phenol (10 g.) was dissolved in water and glycerol (10 c.c.) was added and an aqueous solution of mercuric chloride (6 g.) was next poured in. No precipitate was obtained, but on addition of sodium bicarbonate solution and stirring, a yellowish white precipitate was obtained. On the addition of a small quantity of very dilute hydrochloric acid or a strong solution of sodium chloride the colour changed to white. The same compound was prepared by converting the phenol to sodium phenate by the addition of the requisite quantity of caustic soda and then adding mercuric chloride and sodium bicarbonate. The addition of glycerol in the case of sodium phenate is not necessary. The white precipitate obtained in either case was filtered and thoroughly washed with water. It was found to be partially soluble in alcohol and also in hot water. It was therefore first exhausted with boiling alcohol in an invert condenser and the alcoholic solution filtered through a hot filter. On cooling a white crystalline precipitate was obtained. This was recrystallised from hot alcohol, dried, analysed and tested and were found to be *p*-hydroxyphenylene mercuri-chloride prepared by Dimroth (*Ber.*, 1898, **31**, 2154).

The substance dissolves in caustic soda without decomposition and melts at about 219°.

The residue after extraction with alcohol was then dissolved in hot water and filtered through a hot filter. The solution on cooling deposited white crystals which were found to be *o*-hydroxyphenylene mercuri-chloride (m. p. 133°), $(OH)\cdot C_6H_4\cdot HgCl(2)$ prepared by Dimroth (*Ber.*, 1898, **31**, 2154). (Found: Hg, 60·01 ; Cl, 9·98. C_6H_5OHgCl requires Hg, 60·94 ; Cl, 10·77 per cent.).

o-Phenylenedioxy-dimercuri-chloride, $C_6H_4(OHgCl)_2$

Catechol (4 g.) was dissolved in an excess of water and glycerol (10 c.c.) was added and then an aqueous solution of mercuric chloride (16 g.) was poured in. A solution of sodium bicarbonate (5 g.) was then gradually added when effervescence occured and a green precipitate was formed. It was then filtered off and thoroughly washed with water and dried.

It was found to be insoluble in alcohol, chloroform and other organic solvents. It was very readily decomposed by caustic soda and ammonia and was insoluble in dilute mineral acids. It dissolved in conc. sulphuric acid giving a green solution and decomposed at 150° to a black powder.

Judged by the above properties and analysis the substance appears to be *o*-phenylene dioxy-di-mercurichloride. (Found: Hg, 68·20; Cl, 13·74. $C_6H_4O_2Hg_2Cl_2$ requires Hg, 69·15; Cl, 12·22 per cent.).

It is to be noted that catechol has not yet been mercurated. Dimroth reported (*Ber.*, 1899, **32**, 758) that catechol did not form any mercury derivatives but only reduced their mercuric acetate. The preparation of oxy-mercuri-chloride of catechol by this method is therefore a distinct step in the preparation of mercury compounds of catechol.

m-Phenylenedioxy-dimercurichloride.

Resorcinol (5 g.) was dissolved in excess of water and then on the addition of glycerol (15 c. c.), mercuric chloride (20 g.) and finally sodium bicarbonate solution (6 g.), a voluminous white precipitate was produced. The precipitate was allowed to settle, filtered, thoroughly washed with water and dried. The substance was found to be insoluble in alcohol, acetone, ether, chloroform and other organic solvents. It was also insoluble in caustic soda which readily decomposed it. The substance decomposed at 210° without melting.

Analysis and the properties of the compound would make it to be *m*-phenylene dioxy-dimercuri-chloride. (Found: Hg, 69·80; Cl, 11·60. $C_6H_4O_2Hg_2Cl_2$ requires Hg, 69·15; Cl, 12·22 per cent.)

It is to be noted that Dimroth and Metzger (*Ber.*, 1902, **35**, 2853) prepared by the mercuric acetate method a mercuri-chloride derivative of resorcinol having the formula $C_6H_3(OH)_2.HgCl$ in which the HgCl radical entered the nucleus which had properties different from the oxymercuri-chloride prepared by us. Dimroth's compound is soluble in chloroform and melts at 123° whilst our compound is insoluble in chloroform and decomposes at 210° without melting. The above authors have also prepared a di-mercuri-chloride derivative (*loc. cit.*) of resorcinol $C_6H_2(OH)_2(HgCl)_2$ which decomposes at 200° without melting and is soluble in ether whilst our compound is insoluble in ether.

Orcinol dioxy-dimercurichloride, $(1)CH_3.C_6H_2(OHgCl)_2(3:5)$—Five gm. of orcinol (in excess of water), 20 gm. of mercuric chloride, 5 gm. of sodium bicarbonate and 5 c.c. of glycerol were taken. The mixture was left undisturbed for about an hour for allowing the precipitate to settle. It was then filtered and thoroughly washed with water. The substance was found to be insoluble in ordinary organic solvents. It dissolves completely in hot dilute nitric and hydrochloric acids and also in hot glacial acetic acid. It is decomposed by caustic soda. The substance decomposes completely at 210° without melting.

The substance would correspond to the formula for orcinol dioxy-di-mercurichloride as judged by its analysis and properties. (Found : Hg, 67·74 ; Cl, 12·22. $C_7H_6O_2Hg_2Cl_2$ requires Hg, 67·51 ; Cl, 11·93 per cent.).

o-*Methoxyphenyleneoxy-mercurichloride*, $(1)CH_3O.C_6H_4.OHgCl(2)$. —Guaiacol (3 g.) was dissolved in alcohol and then glycerol (20 c.c.) and a solution of sodium bicarbonate (2 g.) were added to it. An aqueous solution of mercuric chloride (6 g.) was next poured in. The deep yellow precipitate was filtered, washed with alcohol and then with water. The substance was found to be insoluble in alcohol, chloroform, acetone and benzene. It is decomposed by caustic soda and ammonia solutions. It dissolves in excess of conc. hydrochloric acid and also in warm conc. nitric acid. It decomposes at 130° without melting. Analysis and the properties of the compound point out its constitution to be *o*-methoxy phenylene oxy-mercuri-chloride. (Found : Hg, 56·22; Cl, 8·95. $C_7H_7O_2HgCl$ requires Hg, 55·85; Cl, 9·87 per cent.). Efisio Mameli (*Gazzetta*, 1922, **52**, *ii*, 23) obtained guaiacol 4:6-dimercuri-dichloride as a white crystalline powder (by the mercuic acetate

and sodium chloride method) which decompses at 179°-180° and is therefore different from our compound.

Phloroglucinol tri-oxy-tri-mercurichloride, $C_6H_3(OHgCl)_3$.

One gm. of phloroglucinol, 12 gm. of sodium bicarbonate, 6 gm. of mercuric chloride and 2 c.c. of glycerol were taken. In this case a white precipitate was formed which on filtration and washing assumed a light yellow colour. The substance is soluble in conc. hydrochloric acid with decomposition but insoluble in dil caustic soda. The powder decomposes at 160° without melting. (Found: Hg, 71·93; Cl, 12·41. $C_6H_3O_3Hg_3Cl_3$ requires Hg, 72·39; Cl, 12·79 per cent.).

No mercurichloride derivative of phloroglucinol is known, a mercuri-acetate compound only being obtained by Lyes (*J. Pharm. Chim.*, 1905, **6**, 388). The oxy-mercuri chloride prepared here is therefore a new mercury compound of phloroglucinol.

p-*Phenylene dioxy-di-mercurichloride*, $C_6H_4(OHgCl)_2$.

As regards quinol, Dimroth (*Ber.*, 1902, **35**, 2853) has reported that it does not form a mercury compound with mercuric acetate but is simply oxidised to quinhydrone. Using our method we have been able to prepare an oxy-mercuri-chloride derivative of quinol but owing to its ready oxidisability quinol is partially oxidised to quinone (and hence to quinhydrone) which is recognised by its characteristic odour. The quinone partly reduces mercuric chloride to mercurous chloride and even to metallic mercury when the reaction is very vigorous. The resultant product is therefore not pure oxy-mercurichloride, and as it is not soluble in ordinary organic solvents it was not possible to purify it. Nevertheless this method is an improvement over Dimroth's in the fact that a distinct mercurichloride of quinol is actually formed though not in a pure condition.

Four gm. of quinol, 16 gm. mercuric chloride, 5 gm. of sodium bicarbonate and 10 c.c. of glycerol were taken. The quinol was dissolved in excess of water and on the addition of the other substances a white precipitate was formed. The precipitate was allowed to settle and then filtered and washed with alcohol and water.

The white precipitate obtained as above was found to be insoluble in alcohol, chloroform and other organic solvents. It is readily decomposed by caustic soda and ammonia. It is insoluble in dil.

mineral acids. It decomposes at about 160° without melting. The substance on analysis and as regards properties was found to contain *p*-phenylene di-oxydi-mercuri-chloride. (Found: Hg, 75·48; Cl, 15·16. $C_6H_4O_2HgCl_2$ requires Hg, 69·15; Cl, 12·22 per cent.).

That the substance is not pure *p*-phenylene di-oxy-dimercuri-chloride is judged by the fact that the mercury and chlorine are too high owing to the reduction of oxy-mercurichloride partly to mercurous chloride which cannot be avoided.

Amino-Compounds.

Most of the aromatic amines form white crystalline additive derivatives with mercuric chloride alone. It has been shown that if sodium bicarbonate be added beforehand yellow mercury derivatives of the primary, secondery as well as tertiary amines are produced. The addition of glycerol is not necessary. The constitution has already been dealt with (p. 222).

Phenylamine mercurichloride, $C_6H_5NH.HgCl$.

Aniline (3 g.) was dissolved in alcohol and a solution of sodium bicarbonate (3 g.) was added to it. A hot aqueous solution of mercuric chloride (9 g.) was next poured in when a yellow precipitate was formed. This was filtered off, washed repeatedly with alcohol and then with water. The compound was found to be insoluble in alcohol, ether and chloroform. It dissolved in dil. mineral acids.

Analysis and properties prove the compound to be phenylamine mercurichloride prepared by Forster (*loc. cit.*) by boiling an alcoholic solution of $(C_6H_5NH_2)_2HgCl_2$. (Found: Hg, 61·13. C_6H_6NHgCl requires Hg, 61·13 per cent).

Monomethylaniline mercuri-chloride, $C_6H_5.NCH_3.HgCl$.

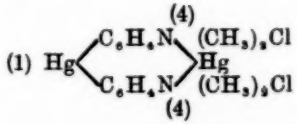
Mono-methylaniline (1 g.) was dissolved in excess of alcohol and a freshly prepared sodium bicarbonate (1 g.) solution was added to it. Alcoholic mercuric chloride (3 g.) was next poured in and the mixture was well shaken. The yellow precipitate was then filtered and thoroughly washed with alcohol.

The substance is an amorphous yellow powder which on exposure to light turns greenish. It is insoluble in water and alcohol and begins to decompose at 108°.

Analysis and properties prove the compound to be monomethylaniline mercuri-chloride. (Found: Hg, 58·13. C_7H_8NHgCl requires Hg, 58·62 per cent.).

This substance is similar in composition and properties to the compound prepared by Pesci (*Gazzetta*, 1892, **22**, *ii*, 32) by the action of hydrochloric acid on methyl-phenyl-mercurammonium hydroxide.

p-Mercurodiphenylenetetramethylmercurodiammonium Chloride.



To a dilute alcoholic solution of dimethylaniline a freshly prepared aqueous solution of sodium bicarbonate was gradually poured in, taking care that no separation of the dimethylaniline took place. An alcoholic solution of mercuric chloride was immediately introduced and the whole thoroughly shaken and then left for an hour or two. The yellow precipitate was then filtered and washed with alcohol. It was then dissolved in boiling alcohol from which on cooling shining colourless crystals were obtained.

The substance is soluble in boiling benzene, alcohol and xylene, and also in water. It begins to decompose at 195° to a bluish substance and at about 215° the colour changes to deep brown.

The substance was identical with *p*-mercurodiphenylenetetramethyl-mecruro-diammonium chloride prepared by Pesci (*Gazzetta*, 1894, **23**, *ii*, 521) by the action of yellow mercuric oxide on dimethylaniline chloride. (Found: Hg, 56·84. $(C_8H_{10}NHgCl)_2$ requires Hg, 56·31 per cent.).

An almost identical compound was obtained by Michaelis and Rabinerson (*Ber.*, 1890, **23**, 2342) by the action of mercuric chloride on mercuro-dimethylaniline and given the formula, HgCl. $C_6H_4.N(CH_3)_2$.

In conclusion we would like to point out that the organo-mercury-compounds prepared by this method might be multiplied to an indefinite extent and the process might therefore be made a general method of preparing aromatic mercury compounds.

PRESIDENCY COLLEGE,
CALCUTTA.

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On Delignification of Jute Fibre.

By

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Investigations to improve the textile quality of bast fibres by the removal of incrusting matters have so long been limited mainly to flax and hemp which are endowed by nature with comparatively long ultimate fibres or cells. The usual methods of removing the lignone matter disintegrate the fibres into ultimate cells (which must be at least 15-20 mm. long to be of value for textile purposes) and cannot therefore be applied to jute. The following experiments were undertaken with the object of delignifying jute, one of the most important crops in Bengal, without reducing it to ultimate fibres and thus extending its usefulness not only as a textile fibre, but also, if delignification can be carried to a sufficient extent, as raw material for various cellulose industries. The textile quality of these treated fibres could however be determined only by actual spinning tests and an exhaustive investigation of their physical properties.

Owing to the secrecy maintained by manufacturers, a review of the methods for the "cottonisation" of flax and hemp cannot be undertaken in this place. It is believed however that most of these processes employ halogens, either in the free state or in chemical combination (Waentig, *Z. ang. Chem.*, 1926, **59**, 1237) or caustic soda of suitable concentration at a high temperature (Waentig, *ibid*, 1923, **56**, 129) as delignifying agent. The application of the above reagents, as also that of the sulphite liquor of paper technologists is too drastic for jute, reducing it to ultimate fibres. The recent process of Cross and Engelstad (E.P. 12945, 1922) of treatment with 6-7 % aqueous sulphur dioxide also reduces jute to ultimate fibres (Cross and Engelstad, *J. Soc. Chem. Ind.*, 1924, p. 256T). It is evident that a less drastic action must be chosen in view of the peculiar chemical and physical constitution of jute.

Chemically, jute belongs to a class of substances known as lignocelluloses. According to Cross and Bevan ("Cellulose," 1918, p. 94) jute consists of cellulose and noncellulose or lignone complexes. The cellulose complex is made up of α-cellulose and β-cellulose,

while the lignone complex contains a diketo-R-hexene group coupled to a hydropyrone group and an aldehydic side-chain similar to that of cinnamic aldehyde (Cross and Doree, "Researches on Cellulose," IV, pp. 156 and 163; also Cross and Engelstad, *Chem. and Ind.*, 1924, p. 254). From a study of the chemical and physiological properties of jute, they conclude that jute is a chemically homogeneous complex. This view is however contradicted by different investigators (Lehne and Schepmann, *Z. ang. Chem.*, 1925, **58**, 97) who maintain that in the so called lignocelluloses, the cellulose fibre is merely incrusted with lignone matter. Wislicenus, on the other hand, finds in lignocelluloses an example of adsorption between colloids, the cellulose and lignone complexes being held together by the forces of surface energy. This view is supported by the microscopical observations of Robinson (*Trans. Roy. Soc.*, 1920, **B 210**, 49).

Physically, jute consists of a bundle of fibres, held together by incrusting matter, the individual fibre being made up of a large number of cells or ultimate fibres, arranged like a telescope and cemented with one another by means of minute quantities of amorphous substances whose chemical nature however remains unknown. These ultimate fibres are again made up of a large number of parallel "fibrills," whose axes may or may not lie in the direction of the cell, these "fibrills" being again made up of the combination of a number of parallel chain of crystals (Herzog, *Zeit. ang. Chem.*, 1926, **39**, 298). In any chemical treatment of the fibre it is therefore necessary that this cementing matter should remain as far as possible unaffected and thus prevent the progressive disintegration of the fibre. This is evidently not the case in the usual methods of delignification. Further, owing to the susceptibility of cellulose to the action of strong acids and alkalis, their use has to be avoided. As a milder reagent, treatment with aqueous solution of neutral sodium sulphite (Keebra process) under great pressure suggest itself, but under these conditions, water hydrolyses the fibre. We have therefore turned to mildly acidic phenols as a suitable solvent for the lignone complex.

The solubility of lignone matter in phenol was first observed by Bühler (D.R.P. 94467, 1897; *Zeit. Ang. Chem.*, 1898, **11**, 119). A similar patent was taken by Kalb & Schöller in 1920 (D.R.P. 365287). while the influence of hydrochloric acid as a catalyser was observed by Hartmuth (D.R.P. 326705 and 328783, 1919). Special mention

may be made of the work of Hillmer (*Cellulose-chemie*, 1925, **6**, 169) who investigated the action of polyhydroxy and substituted phenols on lignone separated by Wilstätter's method and also on wood meal. He found that polyhydroxy phenols were good solvents for lignone and that iodine acted as a better catalyser than hydrochloric acid. But the effect of the solvents on the structure of the fibre or their action on the lignone or cellulose complex in lignocelluloses was not investigated. Cross and Doree on the other hand found that a compound of jute with phlorogucinol was highly resistant to the action of 42% hydrochloric acid and was presumably a homogeneous chemical substance, the lignone complex being unlikely to be separated from cellulose by the use of solvents ("Cellulose Researches," IV, p. 169). It was therefore necessary to investigate if incrusting matters of jute could actually be removed by treatment with phenols.

Solvent Action of Phenols.

A few preliminary experiments with excess of phenol, resorcinol, *m*- and *p*-cresols and creosote showed that the lignone complex of jute was more or less removed by all these reagents at their boiling temperatures. In the selection of the solvent, care has to be taken that it should have the least possible effect on the cellulose constituent. On treating cellulose (quantitative filter paper) with creosote at high temperature and under pressure (Exp. 9, Table I *b*) it was found that the loss in the weight of cellulose amounted to only 1 per cent.

This led to the adoption of creosote as a suitable solvent, beechwood creosote (Merck) having been used for the purpose of these investigations.

It has to be understood however that the mechanism of solution is by no means a purely physical one. Cross and Doree ("Cellulose Researches," IV, p. 160) observe that chemical action takes place between lignone and phenols, the compounds being extremely stable. Hillmer (*Cellulose-chemie*, 1925, **6**, 180) explains the stability by assuming a condensation product with a ring formation. This lignone-phenol derivative apparently dissolves in excess of the solvent.

Prevention of Disintegration into Ultimate Fibres.

While treating jute with creosote or with other phenols in the autoclave, it was found that the fibre became very brittle. This was obviously due to the acidic nature of the phenols, converting the

cellulose into hydrocellulose. The addition of the basic substances had the desired effect in preventing the disintegration.

It will be observed from the following table that maximum effect is obtained by mixing creosote with 10% of its volume of pyridine (Exp. 4). The reduction in the weight of the fibre by the use of larger amount of pyridine is mainly due to the attack on cellulose. It will also be noted (Expt. 6, Table I*a*) that when jute is treated with pyridine alone, the reduction in weight of the fibre amounts to 20%, of this only 9·69% being due to the removal of lignone (taking 19·69 % as the lignone content of raw jute), the remaining 10·31% being apparently removed from the cellulose complex. It is to be noted that neither the structure nor the tensile strength of jute seriously suffers from this treatment, the cementing matter remaining practically unaffected. Hillmer (*loc. cit.*, p. 183) observed that addition of pyridine serves to lower the solubility of cellulose in phenols. In contrast with this observation, it is found that pyridine attacks the cellulose complex, though the structure of the fibre is not thereby affected. When pyridine is substituted by aqueous ammonia, the fibre-strength is considerably reduced, due to the hydrolytic action of water.

Investigations into the hydrolysis of the fibre by water showed that at 100°, the fibre was very little affected. But at 193-195°, the loss in weight was considerable, and the fibre was reduced to pulp. In treating the fibre at high temperature, the use of water was therefore avoided, and rectified spirit was used in exerting pressure in the autoclave.

TABLE I.

Effect of the addition of basic substances.

Temperature 193-195°; Pressure 28-30 atmospheres.

Time of treatment 4 hours.

Solvent 50 c.c. creosote for 1 gm. of jute.

Expt.	Basic subst.	% Basic subst. in solvent.	Loss in wt. of jute %	Lignin present %	Methyl no.	Tensile strength.
1	Pyridine	60	30·06	...	3·5	...
2	,,	40	25·6	3·8	...	...
3	,,	20	24·4	4·2	3·5	Good
4	,,	10	23·0	4·4	3·8	Good
5	,,	0	17·4	6·5	4·73	Bad

TABLE I(*a*).

Expt.	Basic subst.	C.c. of basic subst. to 1 gm. of jute.	Loss in wt. of jute %	Lignin present. %	Tensile strength.
6	Pyridine (no creosote)	80	20·4	10	Good
7	Aqueous ammonia	2	17·6	5·4	Bad
8	Aniline	2	16·4	...	...

The effect of the addition of pyridine on cellulose will be clearly seen from the following data obtained by the action of creosote and creosote-pyridine on quantitative filter paper (cellulose).

TABLE I(*b*).

Effect of the addition of pyridine on cellulose.

Temperature 193-195°; Pressure 28-30 atmos.
Time of treatment 4 hours.

Expt.	Vol. of creosote to 1 gm. of jute.	Vol. of pyridine added to creosote.	Loss in weight %	Strength of paper.
9	100 c.c.	*nil*	1	Brittle
10	100 c.c.	30 c.c.	21·8	Fair.

Optimum Conditions for the Application of Creosote-Pyridine Mixture.

Having determined the means of preventing disintegration, we next undertook to ascertain the optimum conditions for the removal of the incrusting matters without breaking down the fibre. Preliminary experiments to remove the lignone by treatment with creosote at 195° and at ordinary pressure showed that the amount of lignone removed in the course of 4-5 hours was practically negligible (Expt. 11, Table II). After 18 hours' treatment, the jute showed a loss of 22% in weight, but still contained 6·8 % lignone (lignone content in raw jute being 19·69%) and was of apparently good tensile strength. Apparently, the cellulose complex was not absolutely unaffected by this prolonged treatment, as the above figures show. The progress in delignification was followed by means of the usual colour tests for lignocellulose and for cellulose with the help of microscope.

TABLE II.

Effect of time of treatment on delignification.

100 C.c. creosote for 1 gram of jute.
Temperature 195°; Pressure, ordinary.

Expt.	Time (hrs.)	Loss in wt. of jute. (%)	Lignone content. (%)	Tensile strength.
11	4	5·0	14·6	Good.
12	10	12·0	...	Good.
13	18	22·0	6·8	Good.

The following experiments represent attempts to reduce the time of treatment and to secure more effective delignification first by regulating temperature and pressure and secondly by the use of suitable catalyser.

From the following table (Table III) it will be noted that maximum delignification was obtained at a temperature of 193-195° and a pressure of 28-30 atmos. in the course of 4 hours without serious injury to the fibre. This may be contrasted with the results of Experiment 11 (Table II) where only slight delignification was obtained at ordinary pressure and at the same temperature (193-195°). Further increase in pressure with consequent rise in temperature resulted in diminishing the strength of the fibre.

It will be observed from Expts. 14 and 15 that delignification increased with rise in temperature. Further increase in temperature however affected the fibre adversely. In applying high pressure and temperature the use of pyridine was found necessary to prevent disintegration.

TABLE III.

Effect of temperature and pressure on delignification.

Time of treatment—4 hours.

Expt.	Temp. C.	Press. (atmos).	Creosote (c.c) for 1 gm. jute.	% of Pyrid- in creo- sote.	Loss in wt. %	Lignone content. %	Tensile strength.
14	160	1	100	60	2	...	...
15	195	1	100	...	5	14·6	Good
16	170	18	50	20	...	12·76	Good
17	180	22	50	20	14·3	9·7	Good
18	195	28-30	50	20	24·4	4·2	Fair
19	205	35	50	20	25·5	3·8	Bad

The use of hydrochloric acid and of halogens as catalyser have been investigated by different authors. In the case of jute, the use of hydrochloric acid could not be taken into consideration, owing to its hydrolysing action on cellulose. As recommended by Hillmer, iodine, the mildest of the halogens, was chosen for investigation. The application of creosote mixed with varying percentages of iodine showed increased loss in the weight of the fibre with increase in the amount of iodine (Expts. 20-22, Table IV). The fibre became brittle at the same time, owing to the action of hydriodic acid on cellulose. The action of iodine was apparently chemical, the cellulose complex having been seriously affected. To neutralise the action of hydriodic acid, pyridine was added to the mixture of creosote-iodine and experiments were carried on under optimum conditions of temperature and pressure. But it will be noted (Expt. 24 & 25) that the addition of small amounts of iodine did not help delignification. The use of substances which more or less attack cellulose as catalysers suggests that their function is to remove cellulose from the ligno-cellulose complex thus exposing lignone to the action of the solvent.

It has been mentioned that pyridine at high temperature and pressure attacks the cellulose complex to a considerable extent. Pyridine may therefore be expected to behave as a catalyser similar to halogen and halogen acids. From the results of the Expts. 3, 4, and 5 (Table I) this will be seen to be actually the case.

TABLE IV.

Effect of iodine as a catalyser.

Expt.	Vol. creosote (1 gm. jute).	Vol. pyridine.	Iodine (% on jute)	Time (hrs).	Temp. C	Press. (atmos.)	Loss in weight. %	Tensile strength.
20	75 c.c	...	11·8	3¼	145	10	15·1	Brittle
21	100 ,,	...	17·7	4	143	10	18·9	do.
22	125 ,,	...	20·3	3	143	10	20·6	do.
23	125 ,,	...	...	2	143	10	2·0	do.
24	50 ,,	30 c.c.	2	2	200	32	23·3	Fair
25	50 ,,	30 ,,	0	2	200	32	24·4	do

The influence of the time factor on delignification will be seen from the following table as also from Table II. From experiment 32, it will be noted that under optimum conditions of temperature, pressure and time the lignone content of raw jute can be reduced from 19·69% (Expt. 36) to 4·4% without seriously injuring the strength of the fibre.

TABLE V.

Progress of delignification with time of treatment.

Temperature 193-195°. Pressure 28-30 atmos.

Expt.	Time (hours.)	Vol. of creosote for 1 gm. of jute (c.c.)	Vol. of pyridine. (c.c.)	Loss in wt. of jute %	% Lignone content.	Tensile strength.
26	½	125	75	11	...	...
27	1¼	,,	,,	18·1	...	...
28	2	,,	,,	24·4	...	...
29	3	,,	,,	28·5	...	...
30	4	,,	,,	31·2	...	...
31	3	50	5	18·1	5·9	Good
32	4	,,	,,	23	4·4	Fair
33	5	,,	,,	26·3	2·9	Bad.

Analyses of Raw and Treated Jute.

Analysis of the jute cellulose obtained by the above treatment under optimum conditions (Expt. 32) was undertaken and the ash, moisture, lignone, and pentosan contents were determined. The figures may be compared with those obtained from an analysis of raw jute on the one hand and of jute cellulose obtained by chlorine treatment on the other. The results of the analyses of raw and treated jute are shown in the following table.

TABLE VI.

Analysis of Raw and Treated Jute.

Expt.	Raw jute.	Expt.	Treated jute.
34	Ash—0·68%	39	Ash—0·373%
35	Moisture—12·9%	40	Moisture—9·1%
36	Lignone—19·69%	41	Lignone—4·4%
37	Methyl no.—17·82%	42	Methyl no.—3·5%
38	Furfural—11·0% (pentosan)	43	Furfural—8·67% (pentosan).

It will be observed that the lignone matter has been substantially reduced by treatment with creosote-pyridine mixture but the pentosan content in the treated fibre is still high (8·67 per cent. furfural). This may be compared with the furfural content of 8·35 per cent.

which was found by Lehne and Scheppmann in jute cellulose obtained by Cross and Bevan's standard method of chlorine treatment (*Zeit. ang. Chem.*, 1925, **58**, 95). This striking agreement in the furfural content suggests that the mechanism of the reaction of jute with phenols may be similar to that of chlorine (Cross and Bevan, "Cellulose," 1918, pp. 95, 135). Investigations in this direction have not, however, been completed.

Further Refining of the treated Fibre.

The furfural yielding complex (β-cellulose) in the raw jute cellulose obtained by the above treatment may be removed by two methods, namely (1) by heating with 5-6 per cent. NaOH solution, or (2) by treatment with 17·5 per cent. NaOH solution in the cold (Heuser and Bodeker, *Zeit. ang. Chem.*, 1921, **54**, 461). Owing to the susceptibility of the fibre to concentrated alkali, only the first method was employed in these investigations. Addition of a small amount of phenol to the dilute alkali was found useful in improving the colour of the fibre to a certain extent. Analysis of this finally treated fibre gave the following results.

Expt.	
44	Lignone – 2·5%
45	Furfural—4·09% (pentosan)

Evidently the alkali treatment serves to delignify jute further, in addition to the lowering of the furfural yielding complex. The fibre however retains its original colour and is apparently of good tensile strength. The bundle of the fibres breaks down into individual fibres of smaller diameter, owing to the removal of the gummy matter. Observed under the microscope it gives all the standard colour reactions of cellulose, as will be evident from the following table.

TABLE VII.

Reagent.	Cotton.	Raw jute.	Creosote-pyridine treated jute.	Finally refined jute.
Iodine solution	Yellow	Brown	Yellow	Yellow
Zinc chloride-iodine	Violet	Yellowish brown	Violet [1]	Violet [1]
Sulphuric acid-iodine	Blue	Brown	Bluish	Bluish
Phloroglucine-HCl	No coloration	Rose-red	Yellowish [2]	Yellowish [2]

[1] Development of colour takes a little time and is not so uniform as is the case with cotton.

[2] Apparently no change in colour, as the treated fibre is also yellowish.

Finally it may be observed that the production of cellulose fibre from jute lends support to the incrustation theory of the constitution of jute. It appears unlikely that the incrusting matters consist of the lignone-complex only but that the incrustation is formed by a lignone-cellulose complex, held together either by forces of chemical affinity (Cross and Bevan) or of surface energy (Wislicenus). That the incrusting matter is very firmly fixed to the cellulose is evident from the following considerations.

(*a*) While lignone, isolated by treatment with 42 % HCl (Willstätter), dissolves in phenols in a few minute (Hillmer, *Cellulosechemie*, 1925, **6**, 169) it requires several hours to effect the solution of the lignone-complex in jute.

(*b*) Cellulose attacking reagents, such as halogens, halogen acids and pyridine act as catalysers by exposing the incrusting matters to the action of solvents.

(*c*) From a comparison of the figures for loss in weight of the treated fibre and its lignone content it will be noted that a certain amount of cellulose is always affected in the attempt to remove the incursting matter. The want of any fixed proportion between the amount of cellulose and lignone complexes removed suggests that the combination is more of a physical nature (Wislicenus) than of chemical.

Experimental.

Preparation of the Fibre.—The lowest portion (about 1 ft.) was rejected. The fibre was then freed from woody matters and separated as far as possible into individual fibres by mechanical means in order to get uniform results by creosote-pyridine treatment. It was further cut into small pieces and washed by means of soap solution (Pear's soap) in order to free it from dirt and adherent tissues. The difficulty of getting uniform quality of the fibre may further be reduced by loosening the bundle of jute by means of a short preliminary treatment with creosote-pyridine.

Creosote-pyridine Treatment.—Weighed quantity of the fibre prepared as above was taken in a small beaker with the necessary amounts of pyridine and creosote. The beaker was covered with blotting paper to prevent mechanical impurites and was then introduced in an electrical autoclave and placed on a piece of porcelain, pressure being exerted by means of vapours of rectified spirit. After the treatment, excess of creosote was removed by filtration through a Gooch's crucible and the fibre was washed thoroughly by means of

rectified spirit. It was then dried in an air oven at 105° and weighed. The follow data indicate the reduction in weight noted in the previous tables.

Expt.	Initial wt. of dry jute in gms.	Wt. after treatment (dry) in gms.	Reduction. %
1	0·4197	0·2939	30·0
2	0·7040	0·5226	25·6
3	0·8092	0·6104	24·5
4	1·4373	1·1060	23·0
5	0·9290	0·7670	17·4
6	0·4776	0·3800	20·4
7	1·1220	0·9236	17·6
8	0·3958	0·3308	16·4
9	1·6673	1·6460	1·0
10	0·8033	0·6278	21·8
11	0·8815	0·8364	5·1
12	0·7913	0·6948	12·1
13	0·9992	0·7832	21·9
14	0·3790	0·3715	2·0
15	0·8815	0·8364	5·1
17	0·8397	0·7200	14·1
18	0·8092	0·6104	24·5
20	0·3434	0·2914	15·1
21	0·2754	0·2232	18·9
22	0·1744	0·1383	20·6
23	0·3716	0·3662	1·4
24	0·3934	0·3017	23·3
25	0·4450	0·3362	24·4
26	0·2710	0·2408	11·1
27	0·3752	0·3051	18·6
28	0·4450	0·3362	24·4
29	0·3062	0·2188	28·5
30	0·3628	0·3495	31·2
31	0·9215	0·7544	18·1
32	1·4373	1·1060	23·0
33	0·6342	0·4670	26·3

Analysis of Jute.

(1) Moisture was estimated in the usual manner by drying at 105°. The amount in raw jute was found to vary with atmspheric humidity.

Expt.	Wt. of jute (air dry).	Wt. of jute dried at 105°.	Moisture %	
35	1·5341 gms.	1·3240 gms.	13·1	12·9 (mean)
	0·1934 gms.	0·1686 gms.	12·7	
40	0·1348 gms.	0·1220 gms.	9·1	

(2) Ash was estimated by igniting the jute in a platinum crucible.

Expt.	Wt. of dry jute.	Wt. of ash.	% of ash on dry jute.
34	3·6176 gms.	0·0042 gms.	0·68
39	0·2680 gms.	0·001 gms.	0·373

(3) Lignone in jute was estimated (*a*) indirectly by the determination of methyl number, and (*b*) directly by treatment with 42 % hydrochloric acid (Willstätter and Zechmeister, *Ber.*, 1913, **46**, 4201). The simple method of König and Becker of treatment with 72 % sulphuric acid was not followed as lignone is believed to be more or less affected by the acid of this concentration.

(*a*) Methyl number was determined by the method of Benedikt and Bamberger (*Monatsh.*, 1894, **15**, 509). By treatment with hydriodic acid according to the well known Zeisel method. As one gram of AgI corresponds to 0·06383 gm. of CH_3, the methyl number (calculated on 1000 gms. of the fibre) is given by the following formula:—

$$\text{Methyl no.} = \frac{0{\cdot}06383 \times N \times 1000}{A}$$

Where N is equal to the quantity of AgI (precipitate) in grams and A is equal to the quantity of fibre used (grams). The experimental data are given below.

Expt.	Wt. of dry fibre in gms.	Wt. of AgI in gms.	Methyl no. on dry fibre.
1	0·2139	0·0125	3·73
3	0·3181	0·0174	3·5
4	0·3452	0·0205	3·8
5	0·2719	0·0201	4·73
37	0·3076	0·0864	17·66
42	0·3181	0·0174	3·5

(*b*) *Estimation of lignone by treatment with highly concentrated* HCl.

Owing to the possibility of the methoxy groups being partly split off by the creosote treatment, determination of methyl number was given up in favour of the direct method of Willstätter and Zechmeister for the estimation of lignone. This method had the additional advantage of being less costly and required less attention. Owing to the difficulty of getting 42 % HCl we adopted the modification of Kroll (Schwalbe and Sieber, " Betriebs-Kontrolle in der Zellstoff and

Papier-Industrie ", p. 102) and generated highly concentrated HCl by passing HCl gas, cooled in a condenser with ice water, in a mixture of jute and ordinary concentrated HCl, this mixture being at the same time cooled in ice. After allowing it to stand for 24 hours it was diluted to ten times its original volume with water, warmed and filtered through a Gooch's crucible and weighed after drying to constant weight. The cellulose was completely hydrolysed while the non-cellulose matter was left unaffected.

Expt.	Wt. dry jute in gms.	Wt. of lignone in gms.	% of lignone.
2	0·110	0·0042	3·8
3	0·1322	0·0056	4·2
4	0·1452	0·0062	4·4
5	0·2942	0·0196	6·5
6	0·1486	0·0148	10·0
7	0·2204	0·0120	5·4
11	0·1902	0·0278	14·6
13	0·2820	0·0194	6·8
15	0·1902	0·0278	14·6
16	0·1818	0·0234	12·76
17	0·2288	0·0222	9·7
18	0·1322	0·0056	4·2
19	0·1142	0·0044	3·8
31	0·1288	0·0076	5·9
32	0·1452	0·0062	4·4
33	0·1558	0·0046	2·9
36	0·4676	0·0421	19·69
41	0·1452	0·0062	4·4
44	0·1220	0·0030	2·5

(4) For the estimation of furfural yielding complex, the gravimetric method of Tollens and Bödener (*Zeit. für Landwirt*, 1910, **58**, 232) was followed as more accurate than the modification of the same by Ling and Nanji (*Biochem. J.*, 1921, **15**, 466) suitable for volumetric estimation. The conditions recommended by Tollens and Bödener were strictly followed and the fibre was boiled with HCl of sp. gr. 1·06. the furfural in the distillate precipitated as phloroglucide and weighed after drying. The furfural content was estimated from the following formula:—

$$\text{Furfural} = (\text{Phloroglucide} + 0{\cdot}001) \times 0{\cdot}571.$$

Expt.	Wt. of dry jute (gms).	Wt. of ppt. gms.	Furfural % (on dry jute).
38	0·5206	0·1013	11·22
43	0·7137	0·1076	8·688
45	0·3685	0·0254	4·07

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Note on the Action of Neutral Salts in Enzymatic Processes. The Effect of Bromides on Salivary Amylase.

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The effect of neutral salts on the action of amylases has been studied from a fairly long time, and it has been found that there is usually an accelerating action. A summary of the main literature may be found in Falk ("The Chemistry of Enzyme Action," 1924, pp. 106-109; compare also Sherman and Thomas, *J. Amer. Chem. Soc.*, 1915, **37**, 623). This note deals mainly with the so-called anomalous effect of bromides on malt amylase as observed by Thomas (*J. Amer. Chem. Soc.*, 1917, **39**, 1501). This author showed a number of years ago that sodium bromide at high concentrations activate the sacharogenic action of malt amylase, but at low concentrations retard this action, a fact in marked contrast with the effect of chlorides, nitrates or sulphate. No explanation was suggested nor any further results have appeared on this subject so far as the present writer is aware. Since the amylases from different sources vary somewhat in their action, and specially the optimal hydrogen ion concentrations are different for each, it was thought desirable to obtain some data with salivary amylase to see if a similar retarding effect of bromides is obtained or not.

Experimental.

Several samples of the amylase were collected from time to time from the human salivary excretion of the same source according to the method of Cole ("Practical Physiological Chemistry," 1921, p. 189). It was found that the amylase became gradually inactive on standing even at the laboratory temperature which never exceeded 20° during the day so far as its amyloclastic action was considered. Thus a sample of the amylase of a particular concentration gave a chromic period of 25 minutes on the first day, 35 minutes on the third day and over one hour on the seventh day. For the present

experiments therefore it was decided to make a series of experiments on the same day and simultaneously so as to get absolutely comparable results. Two different samples of the enzyme have been used which are denoted by numbers.

The amyloclastic action has been determined by the so-called " Achromic Point " method, in which the chromic period or the time necessary to completely hydrolyse the starch into erythro-dextrin and maltose was obtained colourimetrically in presence of iodine. The sacharogenic action was studied by stopping the enzyme action at a particular time by adding alkali and then determining the reduction of Fehling's solution by Schoorl's (*Zeit. angew. Chem.*, 1899, p. 633) method. This method consists in determining the excess of cupric ion by addition of potassium iodide, acidifying and then titrating the liberated iodine by means of thiosulphate. According to Sutton (" Volumetric Analysis," 1911, p. 331) " results agreeing with gravimetric determinations can be obtained if a fair excess of potassium iodide be used, and if this be added to the alkaline liquid prior to acidification." Concordant results have been obtained by the writer by the use of this method. All the enzymatic experiments were carried out at a temperature of 40°C in a water-bath and in each experiment a volume of starch solution containing 0·1 gram of starch (Kahlbaum's soluble), neutral to litmus, was used.

The first experiment was done to determine the optimal *p*H for the enzyme used in these experiments, because there is a considerable divergence in this value among the recorded results. Thus Ringer and Trigt (*Zeit. physiol. Chem.*, 1912, **82**, 484) give the value 6·0, Olsson (*Zeit. physiol. Chem.*, 1921, **117**, 91) gives it as 6·4. Michaelis and Pechstein (*Biochem. Zeit.*, 1914, **59**, 77) found 6·1-6·2 with a phosphate buffer, whilst Hahn and Michalik (*Zeit. Biol.*, 1921, **73**, 10) found *p*H 6·6 with phosphate and 5·6 with acetate mixture. Cole (" Practical Physiological Chemistry," 1921, p. 187) gives the value 6·7 with phosphate mixture. In Table I, the amyloclastic action of salivary amylase in presence of a phosphate buffer is shown. The total volume was 10 c.c. including 2 c.c. of the phosphate solution. The buffer solution was prepared according to the directions given in Clark (" Determination of Hydrogen Ions," 1922). The range between 5·8 to 6·8 was only observed. Some sodium chloride was added to activate the enzyme.

TABLE I.

NaCl=0·2 mole/litre.

Enzyme I=2 c.c.

*p*H.	Chromic period in minutes.	Remarks.
5·8	>55	Not further investigated.
6·0	55	
6·2	50	
6·4	45	
6·6	41	These two chromic periods were practically the same.
6·8	40	

The results show that the optimal *p*H for the amyloclastic action lies in the neighbourhood of 6·7 which is in agreement with that of Cole and Hahn and Michalik. In Table II is shown the effect of sodium chloride on the enzyme activity.

TABLE II.

Enzyme II=4 c.c.

No buffer : Vol.=10 c.c.

Chromic period without NaCl.	Chromic period with NaCl 0·1 mole/litre.
45 Minutes	35 Minutes

From Table II it will be observed that the effect of NaCl is an accelerating one, and hence the enzyme is behaving in a normal way. The following Table III gives the chromic period with different amounts of primary phosphate. The results show that higher concentrations of the primary phosphate have a little beneficial action.

TABLE III.

NaCl=0·2 mol/litre; Enzyme I=2 c.c.

p_H =6·8: Vol. =10 c.c.

Conc. of buffer.	Chromic period in minutes.
0·5 c.c.	45
2·0 c. c.	40

These preliminary experiments showed that the enzyme effect was a perfectly normal one. The two following Tables IV and V now give the amyloclastic action of the amylase in presence of sodium and potassium bromides. Neither any buffer has been added in these experiments, nor any sodium chloride.

TABLE IV.

Effect of Potassium Bromide.

Enzyme II=4 c.c.

Conc. of bromide mole/litre.	Chromic period in minutes.
0·0	45
0·025	47
0·05	50
0·10	40

TABLE V.

Effect of Sodium Bromide.

(Same enzyme as in Table IV.)

0·0	45
0·025	45
0·05	50
0·10	50

These experiments show that with the concentration of the sodium bromide studied, the chromic period was in no case less than that in which no salt was added. With low concentration of potassium bromide a similar result was obtained, but with higher concentrations, an accelerating action was observed. This is in agreement with the observation of Thomas with malt amylase already mentioned. In the following two Tables VI and VII the sacharogenic effect is shown. No buffer was added in these cases also. The reaction was allowed to go on for exactly 15 minutes with enzyme I (Table VI) and 30 minutes with enzyme II (Table VII). The amount of reduction by pure starch has been deducted from the results given.

TABLE VI.

Enzyme I=2 c.c. Vol.=10 c.c.

Conc. of KBr (molar).	Reduction of Fehling's in terms of Cu_2O (milligrams).
0·0	28·596
0·05	19·064
0·15	11·915
0·20	16·681

TABLE VII.

Enzyme II=4 c.c. Vol.=12 c.c.

Conc. of NaBr (molar).	Reduction in terms of Cu_2O (milligrams).
0·0	104·8
0·0208	102·17
0·0416	90·55
0·0832	90·55
0·1664	90·55

These results show that with the concentrations of bromides studied in this paper and with the concentrations of the enzymes, the effect observed is one of depression in the activity of the enzyme. With higher concentrations of the salts possibly an augmenting action would be observed as in the case of amyloclastic action, but this has not been tried in the case of sacharogenic effect.

These experiments extend the results of Thomas to the case of salivary amylase. No satisfactory explanation of these can however be given at this place. A change in the degree of dispersion of the enzymes in presence of the salts may be one of the factors, as well as a change in the iso-electric point of the enzyme (*cf.* Hahn and Harpuder, *Zeit. Biol.*, 1920, **71**, 302), but in some cases the effect is so specific that no general theory which explains all the individual cases can be given. A discussion of the theoretical aspects will be attempted along with further experiments in the next communication.

Summary.

(1) The optimal p_H of salivary amylase is in the neighbourhood of 6·7 with phosphate buffer.

(2) Bromides at low concentrations have a depressing effect on the amyloclastic and sacharogenic action of salivary amylase.

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Essential Oils of Travancore. Part VII.
From the Rhizome of Ginger, *Zingiber officinale*.

By Kishori Lal Moudgill.

Ginger is cultivated, more or less, all over the hilly tracts in Travancore, but its cultivation on a large scale is confined to Ettumanur and Meenachil Taluks and to parts of Kottayam and Chananacherry Taluks. The cultivation commences in the middle of May and the crop is harvested in the middle of December. The green rhizomes contain 70-80 per cent. of water and are dried for export. For this purpose the upper coating is scraped and the scraped ginger is either dried in the sun without further treatment or limed and dried. The latter operation bleaches the root more effectively. The ginger scrapings are generally thrown into a pond along with cattle manure and sweepings, and merely serve to enrich the liquid manure which is used for the next crop. A large quantity of ginger is exported from Travancore but the essential oil obtainable from the roots by distillation with steam, a well-known commercial product, is not manufactured locally. Since there is no specific mention in the literature about the Travancore oil having been investigated, the work described below was undertaken with a view to study the properties and the composition of this oil. While this paper was in manuscript, Sanjiva Rao, Sudborough and Watson (*J. Indian Inst. of Sci.*, 1925, Part X, Vol. VIIIA, 151) published the constants of an oil obtained by them at Bangalore from waste ginger which consists of *rejected ginger* and scrapings. Their results are compared in this paper.

It has been found that the constants of the oil from the local ginger agree very closely with those of the oil obtained from the Jamaica or African rhizomes (Table I). The chief constituent of the oil is zingiberene (70 per cent.), a sesquiterpene hydrocarbon, to the presence of which the high laevo-rotation of the oil is due. On heating or on prolonged contact with air, this compound was found to undergo very great change indicated most prominently by the

change of the laevo-rotation ($[\alpha]_D^{30}$ about $-65°$) to dextro-rotation ($[\alpha]_D^{30}$ about $+5°$).

The oil undergoes the same change but less rapidly. This change has been studied for the oil and the fraction rich in zingiberene.

The optical rotation, determined in this laboratory, for the oil from dry ginger was considerably higher than the maximum rotation recorded by other investigators. As the constants were determined within a few hours of the distillation of the oil and as the optical rotation diminished on keeping, this apparent discrepancy does not prejudice the inclusion of this oil among normal trade oils. The constants of the oil obtained by Rao, Sudborough and Watson (*loc. cit.*) lie, as expected, between those of the oil from ginger alone and the oil from the scrapings (Table I). The higher proportion of alcohols found in the Bangalore oil (ester value after acetylation 49·8) is presumably contributed by the scrapings in the waste ginger (ester value after acetylation 103, author).

A small quantity of oil was obtained from fresh ginger supplied by the Agricultural Farm, near Trivandrum. The constants of the oil show that though it differs from the oils obtained from different samples of dry ginger, this difference is not sufficiently pronounced to exclude this oil from the normal oils of trade. The ginger scrapings, at present utilised only as manure, were found to yield, when distilled in the usual manner, an oil which differs greatly from the oil from the rhizomes. The solubility of the oil and its higher ester value indicate that it is much richer in oxygenated products, and as these are prized in perfumery, it would be of interest to obtain a quantity of the oil so that a more elaborate examination may be made. This work is projected.

Ginger leaves also possess a faint aroma of ginger but no oil could be obtained by distillation with steam.

Experimental.

Two samples of ginger, one fresh and the other one year old, were crushed and distilled with steam (60 lbs. pressure) in a small still of about 10 gallons capacity. The scrapings were distilled separately and without previous treatment.* The oils did not

* It may be mentioned that as the scrapings had to be brought over a long distance a certain amount of rot had set in which may have slightly effected the oil from the scrapings.

possess the pungent taste of ginger which is due to the presence of a ketone, zingerone which is not volatile in steam (*cf.* Nomura, *J. Chem. Soc.*, 1917, **111**, 769; Lapworth, Pearson and Royle, *ibid*, p. 777).

TABLE I.

	Trade (i).	Bangalore.	Author.			
			Fresh dry.	One year dry.	Green.	Scrapings
Yield per cent.	2 to 3	3·54	2·0	1·8	0·8	0·9
Colour	Pale yellow to dark yellow	Golden	Light-yellow	Brownish yellow	Yellow	Brown
D^{27}	0·8740 to 0·8860	(ii) 0·8822	0·8690	0·8733	0·8800	0·8816
$[\alpha]_D^{30}$	−25° to −50°	(ii) −39°·2	−54°·0	−52°·2	−26°·4	−9·85°
n_D^{28}	1·4885 to 1·4950	(ii) 1·4898	1·4891	1·4890	1·4878	1·4862
Acid value	0 to 2	2·1	1·0	0·8	...	1·0
Ester value	1 to 15	7·7	7·4	6·0	...	10·0
Ester value after acetylation.	30 to 45	49·8	30·5	35·9	...	103·0
Solubility. Vols. of 90 per cent. alcohol.	Insol	...	Insol.	Insol	Insol	10 vols.

(i) Parry, "The Chemistry of Essential Oils and Artificial Perfumes," Fourth Edition, Vol, I. p. 99.

(ii) D_{15}^{15}, $[\alpha]_D^{28}$, n_D^{25}

As only small quantities of the oils from green ginger and ginger scrapings were available, the following work was carried out with the oil obtained from dry ginger only.

A small quantity of the oil (50 c.c.) was distilled from the essential oil flask, Schimmel pattern (3 bulbs), under atmospheric pressure

and the following fractions obtained. The yields are compared with those obtained by Thresh and quoted by Parry (*loc. cit.* p. 99) and by Rao, Sudborough and Watson.

TABLE II.

Boiling point.	Yield per cent. Author.	Thresh.	Bangalore p=685 mm.	$[\alpha]_D^{30^\circ}$ (Author).
Below 150°	2·4	5·0	1·4	+53°
150°–200°	9·4	10·0	5·0	+26°
200°–240°	5·4	8·0	12·3	+15°
240°–265°	70·2	60·0	40 0	+ 9°
265°–300°	3·2	7·0	29·8	
Residue (difference)	9·4	10·0	11·5	

It would appear from the rotations of the various fractions recorded above that the oil undergoes change at the high temperatures required for the above distillation under ordinary pressure. Separate portions of the oil were heated for an hour at different temperatures with a view to find out the temperature at which the above changes become markedly noticeable.

TABLE III.

	Temperature of heating.						
	Not heated	100°	125°	175°	190°	240°	
						1 hour	2 hours
$[\alpha]_D^{30^\circ}$	−52°·24	−49°·6	−46·0°	−45·8°	−28°·35	+4°·8	+5°·0

This shows that fractionation under reduced pressure would help to separate the different fractions unaltered, for the oil undergoes but little change below 175°. The oil was fractionated into four fractions (Table IV). The dextrorotation of the first fraction is due to *d*-camphene identified by converting to *iso*-borneol. The major fraction (3), was distilled repeatedly over sodium and, finally an oil with the constants given below obtained (Table V). Values obtained for zingiberene by von Soden and Rojahn are also given.

TABLE IV.

No.	B. pt./3mm.	Yield per cent.	Colour	$d^{30^\circ}_{30^\circ}$ D	$[\alpha]^{30^\circ}_{D}$	$n^{30^\circ}_{D}$
1	50° to 90°	10·0	Colourless	0·8638	+24°·41	1·4600
2	90° to 116°	12·5	,,	0·8708	−37°·25	1·4860
3	119° to 123°	70·0	,,	0·8638	−64°·00	1·4870
4	Above 123°	6·5	Pale yellow			
5	Residue	1·0				

TABLE V.

	Author	von Soden and Rojahn
$[\alpha]^{30^\circ}_{D}$	−64°·0	—
$[\alpha]^{30^\circ}_{D}$	−73°·7	−73°·0
$n^{30^\circ}_{D}$	1·4916	1·49399 at 15°
Specific gravity	0·8690 at 30°	0·8730 at 20°

The nitrosite was obtained by treating freshly distilled zingiberene in petrol solution with a solution of sodium nitrite and glacial acetic acid. A crop of silky fine needles was obtained which melted at 92°—94°. This compound is stated to be unstable by Schreiner and Kremers, m. p. 98°. The crystals obtained above appeared to be quite stable in outward appearance but the melting point was found to vary from time to time, increasing steadily till, after six months, it reached a maximum of 113°. A sample of zingiberene which had been kept in a loose stoppered container for three months did not give a nitrosite. It was found to have altered greatly in constants (Rotation+2°·3, density 0·9345, index of refraction 1·502). This was taken to be due to the exposure to air and the following work was done to study the effect of heating and exposure to air on the compound.

Effect of Heating.—A quantity of zingiberene was heated on a sand-bath to gentle boiling for 45 minutes. The resulting oil was

dextrorotatory and viscous. It was distilled under reduced pressure and the major fraction thus obtained refractionated carefully (Tables VI and VII). Semmler and Becker who studied zingiberene in detail tried the effect of heat on a mixture of zingiberene and isoprene. They obtained a mixture which was found to contain limonene, a bicyclic sesquiterpene which they named *meta*-zingiberene and a diterpene. As has been stated above, a complex change takes place when zingiberene is heated alone. That this is not due to the conversion of zingiberene to *iso*zingiberene is borne out by the constants of the two fractions obtained by refractionating fraction 2. (Table VI.) Apparently zingiberene is altered to another dextrorotatory monocyclic sesquiterpene and not the dicyclic *iso*-zingiberene whose constants would readily differentiate it from the two fractions A and B below (Table VII).

TABLE VI.

No.	B. p. /5mm.	Yield per cent.	$D^{30°}_{4°}$	$n^{27°}_{4°}$	$[\alpha]^{30°}_{D}$
1.	Below 110°	4			
2.	110°–130°	52	0·8902	1·496	+6°·5
3.	Above 130°	12			
4.	Residue	32			

TABLE VII.

	A	B	*iso*Zingiberene.
B. pt. 35° ...	up to 265°	265°–270°	118°/7 mm,
n_D ...	1·492	1·491	1·5062
$D^{27°}_{4°}$ ...	0·8788	0·8835	0·9118
$[\alpha]^{30°}_{D}$ ...	+6°·9	+7°·8	−51·36

Effect of Exposure of Zingiberene to Air.—The following experiments were undertaken with a view to study the changes brought about in zingiberene on exposure to air. Purified zingiberene was divided into three equal portions. One was sealed in a tube (*a*), another kept in a tube of the same size plugged with cotton wool (*b*), and the third in a conical flask similarly plugged (*c*). The constants of these were determined from time to time. As the refractive index could be determined without much loss of material, the changes were followed with the help of the refractometer, the rotations being determined occasionally. A comparison of the graphs of these show that air plays an important part

n the change, the small change undergone by the specimen in the tube (*a*) being attributable to the residual air in it at the time of the sealing. Another experiment confirmed this. The specimen which had been kept in the sealed tube for 19 days without much change was divided into two portions. Air was bubbled through one during eight hours and the other was left plugged for the same period. As expected, the latter underwent but little change whilst the former was found to have altered greatly (rotation + 6·35°, index of refraction 1·5088.) Similar experiments were tried with ginger oil which was found to undergo similar changes, though more slowly than the high percentage of zingiberene would lead one to expect. It is probable that the change is inhibited by the other components of the oil (Tables VIII, IX and X also graphs).

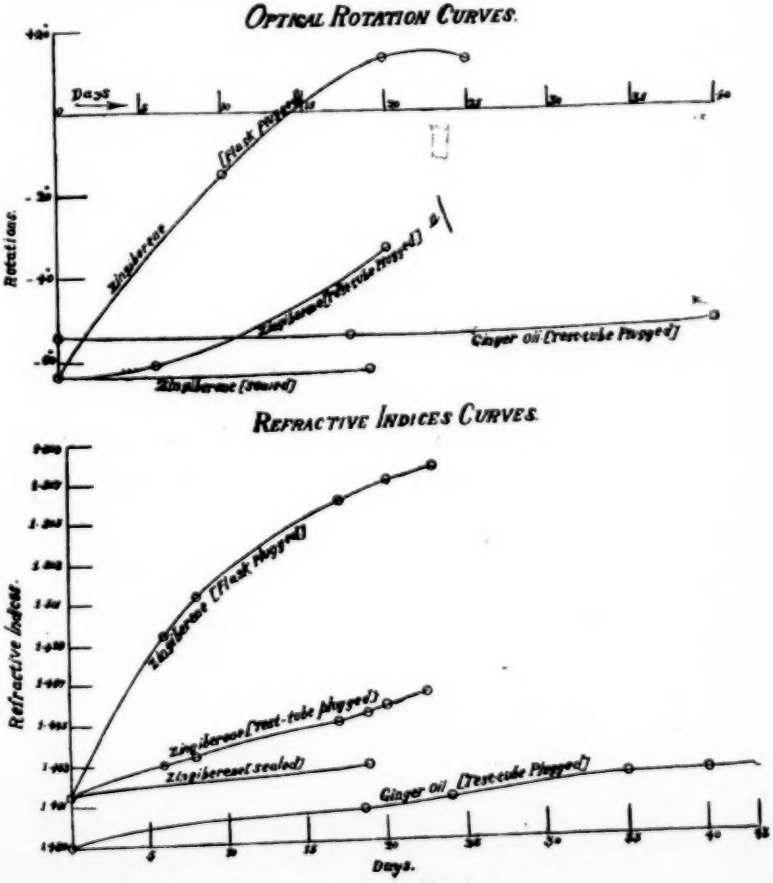

Table VIII.

Effect of Exposure of Zingiberene to Air.

	Sample	Number of days. 0	6	8	17	19	20	23
$n_D^{28°}$	(*a*)	1·4916	...	...	...	1·4918	...	...
	(*b*)	1·4916	1·4930	1·4934	1·4948	1·4954	1·4958	1·4963
	(*c*)	1·4916	1·4995	1·5013	1·5058	...	1·5067	1·5073
$[\alpha]_D^{28°}$	(*a*)	−64·0°	...	...	...	−63·15°	...	...
	(*b*)	−64°·0	−60°·6	...	...	...	−33·2°	...
	(*c*)	−64°·0	−15°·0	...	...	...	+12·5°	+12·5°
$D_4^{28°}$	(*a*)	0·8693	...	...	...	...	...	...
	(*a*)	0·8693	...	...	...	0·8700	...	...
	(*b*)	0·8693	...	...	...	0·8860	...	0·8910
	(*c*)	0·8693	...	...	...	...	...	0·9154

Table IX.

Effect of Exposure of Ginger Oil to Air.

	Sample	Number of days. 0	18	24	35	40	43
$[\alpha]_D^{28°}$	Sealed	−54·0°	...	...	...	...	−54·0°
	Plugged	−54°·0	−53°·75	...	...	...	−50·2°
$n_D^{28°}$	Sealed	1·4890	...	...	...	...	1·4905
	Plugged	1·4890	1·4905	1·4912	1·4921	1·4922	1·4923

Table X.

Exposure of Ginger Oil to Air (air bubbled through).

	Original	Time-hours. 4	8	12	16
$n_D^{28°}$	1·4920	1·4925	1·4931	1·4938	1·4945
$[\alpha]_D^{28°}$	−52°·0	...	...	...	−49°·6

Summary.

1. The essential oil obtained from dry ginger produced in Travancore is normal in character and can be obtained in a yield of 2 per cent. The yield diminished with the age of ginger.

2. Green ginger and ginger scrapings yield an essential oil differing in some respects from the oil from the dry roots.

3. The leaves yield no oil.

4. Ginger oil undergoes change on heating and on prolonged exposure to air. The oil cannot be distilled under ordinary pressure and it should be kept in well-stoppered bottles.

5. Zingiberene changes more readily on heating or on contact with air. At present there is no evidence to show that the changes are identical.

5. On heating at its boiling point, zingiberene yields a monocyclic dextrorotatory sesquiterpene and an undistillable semi-solid residue.

Further work is projected. The thanks of the author are due to the Director of Industries, Travancore, for supplying the materials for distillations and to Mr. P. N. Vridhachalam, B.A., who supervised them.

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On the Alleged Acceleration of Taurocholate Hemolysis by Normal Serum.

By K. C. Sen and Nripendra Kumar Sen.

In a previous paper on the mechanism of hemolysis (Sen and Basu, This *Journal*, 1928, **5**, 1) one of us has shown that the permeability of the membrane of the red blood corpuscles is determined by the colloidal condition of the membrane. The view has also been put forward that the hæmolysis by saponin, bile salts or by soaps is due to the peptisation of some of the membrane constituents such as lecithin or cholesterol, and it was shown both from our experiments as well as from those of others that normal serum inhibits this hemolysis. So far as this inhibiting action of normal serum is concerned, an interesting fact has been observed by Ponder (*Proc. Roy. Soc.*, 1923, **B 95**, 403) several years ago, namely that inhibition is obtained if serum protein is first added to the red cells and then the hemolyte is added, but when the serum is added to a mixture of red cells and hemolyte, an acceleration of hemolysis is observed. This has only been observed in the case of taurocholate hemolysis, but not in the case of saponin hemolysis. This acceleration of taurocholate hemolysis was not explained by Ponder on the basis of current theories, and appears to be quite surprising. Since some emphasis has been put on this phenomenon in a recent article (*Nature*, **1927, 120**, 304) and as no further experiments seem to have been published by Ponder on this acceleration of hemolysis by normal serum, it was thought desirable to make some experiments in this line and curiously enough, we have got quite different results. Owing to the importance of the results of Ponder on theoretical grounds, we quote them below to show their nature.

Table I.

Taurocholate Hemolysis.

	Time of hemolysis.
1 in 3,000 taurocholate	3·5 minutes
1 in 3,000 taurocholate, *plus* 0·025 c.c. serum, added before the addition of red cells...	32 ,,
1 in 3,000 taurocholate, *plus* 0·025 c.c. serum, added 1/2 minute after the addition of cells	0·6 ,,

TABLE II.

Saponin Hemolysis.

	Time of hemolysis.
1 in 30,000 saponin	3·25 minutes
1 in 30,000 saponin *plus* 0·035 c.c. serum added before the addition of red cells	37 ,,
1 in 30,000 saponin *plus* 0·035 c.c. serum added 1/2 minute after the addition of cells	37 ,,

It will be apparent from these tables that in the case of taurocholate there is an acceleration of hemolysis if the serum is added to the mixture of the hemolyte and the red cells. As we have not been able to corroborate this, some of our results will be given.

EXPERIMENTAL.

Ponder in his experiments used human erythrocytes in normal saline. In our experiments we have used mainly sheep's corpuscles both in saline as well as in isotonic sucrose. Some data with human corpuscles are also given later on. Defibrinated blood corpuscles were washed repeatedly with isotonic saline or sucrose as the case may be, and then suspended in it to give a concentration of 1 per cent. All the solutions as well as the glass apparatus used in this investigation were sterilised before use. The method of determining complete hemolysis was by means of a visual comparison with a standard fully hemolysed tube of the same concentration. Where percentage hemolysis has been given, these were also found by a similar method. For comparative purposes, the method was quite good. The hemolytes were dissolved in the proper solutions.

The results are given in the following tables. The experiments given in Tables III to V were all done in isotonic sucrose. The original taurocholate concentration was 5 per cent., total volume 5 c.c., and the temperature 22°. In the second column is given the time in minutes for complete hemolysis.

TABLE III.

	Time of hemolysis.
1. 2 C.c. red cells *plus* 1 c.c. taurocholate	12
2. 2 C.c. red cells *plus* 0·05 c.c. serum *plus* 1 c.c. taurocholate ...	43
3. 2 C.c. red cells *plus* 0·1 c.c. serum *plus* 1 c.c. taurocholate ...	59
4. 2 C.c. red cells *plus* 1 c.c. taurocholate *plus* 0·05 c.c. serum added 1 minute after the addition of the taurocholate	28½
5. 2 C.c. red cells *plus* 1 c.c. taurocholate *plus* 0·1 c.c. serum added 1 minute after the addition of the taurocholate	35

TABLE IV.

	Time of hemolysis. (minutes)
1. 1·5 C.c. red cells *plus* 0·5 c.c. taurocholate	5
2. 1·5 C.c. cells *plus* 0·05 c.c. serum *plus* 0·5 c.c. taurocholate ...	20
3. 1·5 C.c. cells *plus* 0·1 c.c. serum *plus* 0·5 c.c. taurocholate ...	70
4. 1·5 C.c. cells *plus* 0·5 c.c. taurocholate *plus* 0·05 c.c. serum added 2 minutes after the addition of the taurocholate	7½
5. 1·5 C.c. cells *plus* 0·5 c.c. taurocholate *plus* 0·1 c.c. serum added 2 minutes after the addition of taurocholate	18

TABLE V.

1. 1 C.c. red cells *plus* 0·5 c.c. taurocholate	3
2. 1 C.c. cells *plus* 0·5 c.c. serum *plus* 0·5 c.c. taurocholate ...	10
3. 1 C.c. cells *plus* 0·1 c.c. serum *plus* 0·5 c.c. taurocholate ...	35
4. 1 C.c. cells *plus* 0·5 c.c. taurocholate *plus* 0·05 c.c. serum added 3 minutes after the addition of taurocholate	3
5. 1 C.c. cells *plus* 0·5 c.c. taurocholate *plus* 0·1 c.c. serum added 3 minutes after taurocholate addition	3

So long these experiments were made in sucrose solutions. As Ponder's experiments have been carried in saline, similar experiments were also carried out by us. In the following tables, taurocholate is 1 per cent., total volume 5 c.c., and the corpuscle concentration is 1 per cent. All preparations were made in physiological saline.

TABLE VI.

	Time of hemolysis.
1. 2 C.c. red cells *plus* 1 c.c. taurocholate	10 mins.
2. 2 C.c. cells *plus* 0·05 c.c. serum *plus* 1 c.c. taurocholate ...	240 mins.
3. 2 C.c. cells *plus* 0·1 c.c. serum *plus* 1 c.c. taurocholate ...	No hemolysis in 240 minutes.
4. 2 C.c. cells *plus* 1 c.c. taurocholate *plus* 0·05 c.c. serum added 1 minute after the addition of the taurocholate ...	135 mins.
5. 2 C.c. cells *plus* 1 c.c. taurocholate *plus* 0·1 c.c. serum added 1 minute after the addition of the taurocholate ...	About 60% hemolysis in 240 minutes.

TABLE VII.

	Time of hemolysis.
1. 2 C.c. cells *plus* 1·5 c.c. taurocholate	8 mins.
2. 2 C.c. cells *plus* 0·05 c.c. serum *plus* 1·5 c.c. taurocholate ...	About 20% hemolysis in 135 mins.
3. 2 C.c. cells *plus* 0·1 c.c. serum *plus* 1·5 c.c. taurocholate ...	No hemolysis in 150 mins.
4. 2 C.c. cells *plus* 1·5 c.c. taurocholate *plus* 0·05 c.c. serum added ½ minute after the addition of the taurocholate ...	85 % hemolysis in 135 mins.
5. 2 C.c. cells *plus* 1·5 c.c. taurocholate *plus* 0·1 c.c. serum added ½ minute after the addition of the taurocholate ...	35 % hemolysis in 150 mins.

TABLE VIII.

1. 2 C.c. cells *plus* 2 c.c. taurocholate	5½ mins.
2. 2 C.c. cells *plus* 0·05 c.c. serum *plus* 2 c.c. taurocholate ...	150 mins.
3. 2 C.c. cells *plus* 0·1 c.c. serum *plus* 2 c.c. taurocholate ...	No hemolysis in 150 mins.
4. 2 C.c. cells *plus* 2 c.c. taurocholate *plus* 0·05 c.c. serum added 1 minute after the addition of the taurocholate ...	150 mins.
5. 2 C.c. cells *plus* 2 c.c. taurocholate plus 0·1 c.c. serum added 1 minute after the addition of the taurocholate ...	45% hemolysis in 150 minutes.

Several more tables of this nature were obtained but these are not given here. All these experiments were made with taurocholate as the hemolyte. It should be noted that in sucrose solutions more of taurocholate is necessary to hemolyse the same amount of the corpuscles than in saline solutions. Evidently sucrose has an inhibiting action on taurocholate hemolysis. Ponder has shown that in saponion hemolysis, no peculiar behaviour is observed with serum. It was therefore thought desirable to investigate the effect of serum on oleate hemolysis, and Table IX gives the results. The solutions were made in isotonic sucrose. The potassium oleate concentration was 0·025 per cent. and the total volume of the mixture 5 c.c.

TABLE IX.

	Time of hemolysis.
1. 2 C.c red cells *plus* 0·2 c.c. oleate ...	20½ mins.
2. 2 C.c. cells *plus* 0·05 c.c. serum *plus* 0·2 c.c. oleate ...	80% hemolysis in 60 minutes.
3. 2 C.c. cells *plus* 0·1 c.c. serum *plus* 0·2 c.c. oleate ...	Slight hemolysis only in 60 minutes.
4. 2 C.c. cells *plus* 0·2 c.c. oleate *plus* 0·05 c.c. serum added 1 minute after the addition of the oleate ...	36 minutes.
5. 2 C.c. cells *plus* 0·2 c.c. oleate *plus* 0·1 c.c. serum added 1 minute after the addition of the oleate. ...	60 minutes.

So long all the results were obtained with sheep's corpuscles. Since Ponder's work has been mainly done with human erythrocytes, some data of this nature have also been obtained by us. The blood used was obtained from one of the authors, and the corpuscles were defibrinated and washed with saline. The total volume of the mixture was 5 c.c., final concentrations of corpuscles and taurocholate were 0·4 per cent. and 0·06 per cent. respectively, and the temperature 26°. The figures indicate the time for complete hemolysis. All solutions were made in physiological saline.

TABLE X.

		Time of hemolysis.
(1)	Corpuscles + taurocholate	8½ mins.
(2)	Corpuscles + taurocholate + 0·01 c.c. serum added one minute after the addition of the taurocholate	15 mins.
(3)	Corpuscles + taurocholate + 0·02 c.c. serum added one minute after taurocholate	25 mins.
(4)	Corpuscles + taurocholate + 0·03 c.c. serum added one minute after taurocholate	80 mins.

Discussion.

The results given in the foregoing tables will show conclusively that in no case there is an acceleration of hemolysis due to the addition of normal serum, but in every case there is a retardation. It should be stated here however that while making hemolytic experiments with low amounts of corpuscles, in one or two cases an actual acceleration was found to take place, but these results could not be reproduced. It is very difficult to obtain a sharp end point with small amount of corpuscles. This is undoubtedly due to the liberation of hemoglobin which has been shown by Ponder to have a retarding effect on hemolysis. Owing to this fact the time for complete hemolysis may not be exact, but as in each table the results are quite comparative, the conclusion we have arrived at is experimentally true. For this reason, we think that Ponder's results (compare also *Proc. Roy Soc.*, 1927, B **101**, 212) may be due to some particular conditions affecting his experiments and are not true as general cases.

In view of our experimental results, the theoretical difficulty of explaining the action of serum on hemolysis disappears, and the

facts can be made to agree with existing theories. Whatever may be the real explanation of the reaction between the corpuscle surface and the hemolyte, we consider that the effect of serum is one of competition for the erythrocyte surface, because a similar assumption has been found useful in sedimentation and agglutination experiments. P. L. du Noüy ("Surface Equilibria of Biological and Organic Colloids," 1929) has shown that normal serum when examined immediately has a higher surface tension than pure water, and thus has an antagonistic action towards hemolytes like soap, bile salts or saponin which tend to lower the surface tension of water. In the previous pages we have shown that this antagonistic action finds an easy explanation from a purely colloidal point of view. Whether that explanation is right or wrong is another matter, but so far as the present experiments are concerned, they can be explained without assuming any particular difference between taurocholate hemolysis and saponin hemolysis. All that our results show is that the time necessary for complete hemolysis is less when the serum is added to the red cells after the addition of the hemolyte than the time required when it is added before the addition of the hemolyte. This is quite natural, because in the first case, the hemolyte being alone in contact with the surface of the erythrocyte, has been adsorbed to a greater extent and the disintegrating influence of the adsorbed hemolyte has already proceeded to a certain extent. The effect of serum is consequently less marked than in the case where serum is added previous to the addition of the hemolyte. Consequently we believe that there is no essential difference in the mechanism of the hemolytic action of soaps, bile salts or saponin. Our experimental results given in this paper, if corroborated, will show, contrary to Ponder's implied suggestions, that the effect of serum in the inhibition of hemolysis is the same in every case, and that a single view will explain the hemolytic behaviour of saponin, soap or bile salts.

Finally one remark may be made regarding the mechanism of this inhibition by serum about which we have said nothing so long. There is a prevalent view that serum proteins combine with the hemolyte thus making it ineffective. In a recent paper in this *Journal* (Sen and Basu, *loc. cit.*) we have suggested that the serum proteins may have a sensitising effect on some of the colloidal constituents of the cell membrane whereas the bile salts have a peptising effect on them.

Hence the antagonism between these two substances is really an antagonism between a sensitising agent and a peptising agent in diphasic system. From the work of D'Herelle ("Immunity in Natural Infectious Diseases," English Edition, 1924) it seems that the hemolysis by immune sera or that by heterologous sera is very likely due to coagulating action on the membrane constituents. This coagulating action depends upon the particular physico-chemical state of the proteins in the immunised sera and not due to the presence of any new body as was supposed in the previous paper. Consequently normal serum may be assumed to have at least a sensitising effect on the stroma. But from a further study of the effect of normal serum on the erythrocyte surface, specially in sedimentation and agglutination experiments which have been made by us, it appears that this effect does not seem to be a complete explanation of the inhibition observed. It is concluded that apart from this type of antagonism, there is a tendency of the serum proteins to be adsorbed on the surface of some of the membrane constituents, and this adsorption is strong enough to displace the adsorption of the hemolyte from the surface of the stroma. An effect of this nature is evident in the case of some agglutination experiments by heavy metal salts. On this view we can picture the whole process as follows:—The action of the hemolytes is on the stroma, and hemolysis by substances which diminish the surface tension of solutions such as bile salts, saponin or soaps is due to a peptisation of some of the membrane constituents like lecithin or cholesterol. This peptisation is preceded by an adsorption of these hemolytes by the surface. An inhibition of this type of hemolysis can be caused either by sensitising the peptisable constituents so as to make them less easily peptisable or by inhibiting or displacing this adsorption of the hemolyte by the addition of another strongly adsorbable substance. The effect of normal serum appears to be due to both these causes so far as hemolytes of the class of bile salts are concerned. It is doubtful if the serum proteins chemically combine with the hemolytes of this class to produce the so-called non-hemolytic bodies.

Summary.

(1) Sucrose appears to have an inhibiting effect on taurocholate hemolysis of sheep's red blood corpuscles.

(2) Normal serum has been found to inhibit the hemolysis of sheep's erythrocytes by sodium taurocholate both in sucrose as well as

in saline, and by oleate in sucrose. No accelerating influence of serum has been observed in the case of taurocholate hemolysis, and Ponder's results in this line have not been corroborated.

(3) The view has been put forward that the hemolysis of red-blood corpuscles by saponin, soaps or bile salts is due to a peptising influence of these substances on some of the membrane constituents, and that there is no essential difference in the mechanism of hemolysis by saponin, soaps or bile salts. The action of normal serum is also of the same nature in presence of all these peptising hemolytes.

(4) The effect of normal serum on hemolysis appears to be two-fold. Firstly, owing to a sensitising action on some of the membrane constituents it makes them less easily peptisable, and secondly, owing to its great adsorption on the surface of the stroma, it displaces the adsorbed hemolyte from the cell surface. When present before the addition of the hemolyte, it may hinder the adsorption of the hemolyte to any extent depending on its concentration. Simply the sensitising influence of the normal serum is not a sufficient explanation of the observed antagonism between serum and hemolyte, as was assumed to be the case in the previous paper.

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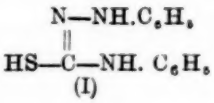
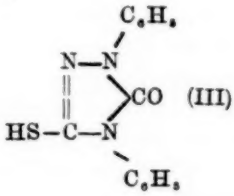
Studies on Oxidation. Part I. Action of Ferric Chloride and Hydrogen Peroxide on Thiosemicarbazones and the Synthesis of Thiodiazoles and Triazoles.

By Satish Chandra De and Satyendra Kumar Roy-Choudhury.

The observations of Merckwald (*Ber.*, 1892, **25**, 3098; 1899, **32**, 1081) that certain 1:4-disubstituted thiosemicarbazides, for example, $C_6H_5.NH.NH.CS.NH.C_6H_5$, can exist in two stereoisomeric forms (I) and (II), which yield triazole and thiodiazole derivatives. (III and IV), with carbonyl chloride, thus:



(I)



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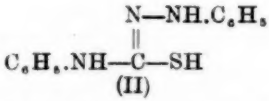

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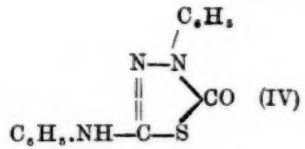
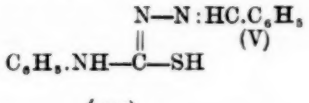


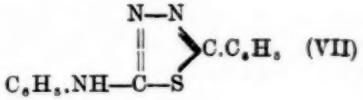
(IV)

probably led Young and Eyre (*J. Chem. Soc.*, 1901, **79**, 54) to suppose that the aldehyde-thiosemicarbazones, though as such unknown to exist in two different modifications, might yield two different products, (VII and VIII) reacting in both of its *syn* and *anti* forms, (V) and (VI), with an oxidising agent, thus:

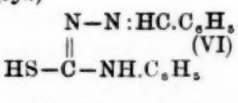


(V)

(*syn*)

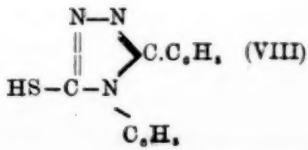


(VII)



(VI)

(*anti*)

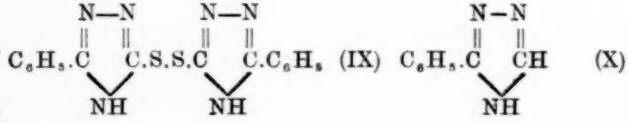


(VIII)

Young and Eyre (*loc. cit.*), however, observed that the product of the oxidation of benzylidene-thiosemicarbazone with ferric chloride consisted entirely of a thiodiazole derivative together with a trace of a higher melting alkali soluble product which they suspected to be a mercaptotriazole.

In the present work Young and Eyre's researches have been followed on an extensive scale taking a large number of thiosemicarbazones, but in no case could we trace the formation of a mercaptotriazole. Our next attempt was to find out a suitable oxidising agent with which the formation of the much expected mercaptotriazoles might be possible and the oxidising agent which answered our purpose has now been found in hydrogen peroxide.

The oxidation of the thiosemicarbazones with hydrogen peroxide takes place more easily and energetically than that with ferric chloride: in the latter case no reaction appears to take place in the cold, whereas the thio-compounds are oxidised by aqueous or alcoholic hydrogen peroxide even in the cold and in some cases the reaction is so violent that it becomes necessary to cool the reaction mixture during the addition of the oxidising agent (see Experimental part). The product is generally a disulphide of a mercaptotriazole, for instance (IX),

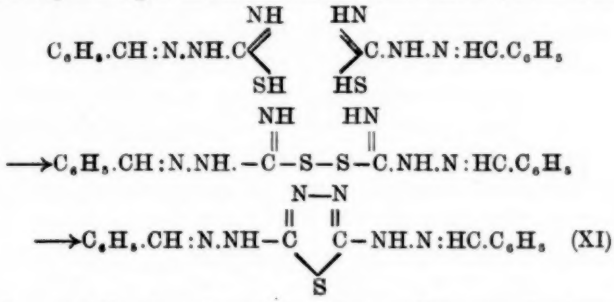


In one or two experiments there has also been obtained a substance which is free from sulphur and which may have been derived from the disulphide (Busch and Bauer, *Ber.*, 1900, **33**, 1067), as the result of further oxidation, the sulphur being eliminated as sulphur dioxide. The formation of the sulphur free compound (formula X), can be checked by careful addition of the calculated quantity of hydrogen peroxide and by allowing the temperature not to rise too high during addition.

It is now evident from the behaviour of the benzylidene-thiosemicarbazones towards hydrogen peroxide that they can react in either of the two possible stereoisomeric forms in presence of a suitable oxidising agent.

Hitherto we have only dealt with the two possible forms of compounds that can be derived from the two stereoisomeric forms of

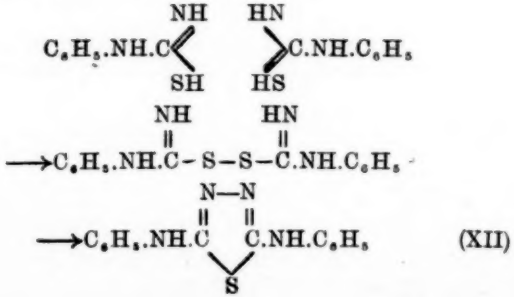
aldehyde-thiosemicarbazones. Leaving aside the question of stereo-isomerism the oxidation may be supposed to proceed in an entirely different way leading to the formation of a thiodiazole (formula XI).



Such a reaction is not possible so long as the azomethane group is present, the hydrogen atom of which is extremely reactive (Pechmann, *Ber.*, 1894, **27**, 1679; Wedekind, *Ber.*, 1897, **30**, 444; Young, *J. Chem. Soc.*, 1900, **77**, 224; Busch and Walther, *Ber.*, 1903, **36**, 1360). The reaction, therefore, takes the course as represented by formula (V) or (VI).

It was next thought that if the reactive hydrogen atom could be avoided as in the case of the ketone-thiosemicarbazones the reaction might be expected to proceed in the manner just described. To achieve this end several acetone-thiosemicarbazones were oxidised with hydrogen peroxide. The product of oxidation consists, as we expected, of thiodiazole derivatives different from those represented by formula (VII).

Thus we find that acetone-thiosemicarbazones can react with oxidising agents similarly as substituted arylthiourea which, as has been shown by Hector (*Ber.*, 1889, **22**, 1177; 1892, **25**, 1578) are oxidised by hydrogen peroxide to thiodiazole derivatives (formula XII).

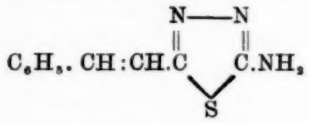


Experimental.

Oxidation of Thiosemicarbazones with Ferric Chloride.

5-Phenyl-2-amino-1 : 3 : 4-thiodiazole.—Benzylidene-thiosemicarbazone was oxidised with ferric chloride according to the direction of Young and Eyre (*loc. cit.*) and the product consisted exclusively of 5-phenyl-2-amino-1 : 3 : 4-thiodiazole hydrochloride (m.p. 213°-214°). No trace of a substance of higher melting point as described by these authors could be obtained even by altering the condition of the reaction.

5-Styryl-2-amino-1 : 3 : 4-thiodiazole.



Cinnamylidene-thiosemicarbazone was oxidised as before in aqueous suspension. The colourless solution obtained on heating the mixture for 10 mins. did not deposit any crystals on cooling. The free base was precipitated along with ferrous hydroxide by ammonia, and from the solid residue the base was extracted with alcohol from which crystals separated on cooling. Recrystallised from alcohol it melts at 260°-261°. (Found : N, 20·72. $C_{10}H_9N_3S$ requires N, 20·68 per cent.).

5-Salicyl-2-anilido-1 : 3 : 4-thiodiazole.—The oxidation was carried out as before with salicylidene-4-phenylthiosemicarbazone when a black solid product was obtained. The colour was partly removed by washing with ether and benzene. Crystallised from benzene with the addition of animal charcoal it formed white crystals, m.p. 190°-191°. (Found : N, 15·57. $C_{14}H_{11}ON_3S$ requires N, 15·51 per cent.).

5-m-Nitrophenyl-2-anilido-1 : 3 : 4-thiodiazole.—It was obtained from the oxidation of *m*-nitrobenzylidene-4-phenylthiosemicarbazone. The insoluble product was filtered from the mother-liquor and crystallised from acetic acid in yellow rectangles, m.p. 249°-250°. (Found : N, 18·82. $C_{14}H_{10}O_2N_4S$ requires N, 18·79 per cent.).

Acetyl Derivative.—The above thiodiazole was heated with acetic anhydride for 10 mins. On cooling crystals separated which were recrystallised from acetic acid, m.p. 246°. (Found : N, 16·62. $C_{16}H_{12}O_2N_4S$ requires N, 16·47 per cent.).

5-p-*Toluidino*-2-*phenyl*-1 : 3 : 4-*thiodiazole*.—Benzylidene-4-*p* tolylthiosemicarbazone (m.p. 165°) was oxidised in alcoholic solution. On cooling white crystals of the thiodiazole were obtained. Crystallised from alcohol in needles it melts at 198°-199°. (Found : N, 15·94. $C_{15}H_{13}N_3S$ requires N, 15·73 per cent.).

Acetyl derivative.—It was prepared in the usual way and crystallised from alcohol in white rectangles, m.p. 155°. (Found : S, 10·61. $C_{17}H_{15}ON_3S$ requires S, 10·35 per cent.).

5-p-*Nitrophenyl*-2-p-*toluidino*-1 : 3 : 4-*thiodiazole*.—Prepared from the oxidation of *p*-nitrobenzylidene-4-*p*-tolylthiosemicarbazone (m.p. 201-202°). After heating for 10 mins. the alcoholic solution became colourless and from the solution on cooling crystals were obtained which when crystallised from acetic acid melt at 197°-198°. (Found : N, 17·82. $C_{15}H_{11}O_2N_4S$ requires N, 17·94 per cent.).

Acetyl derivative.—Prepared in the usual way it crystallises from alcohol in almost white needles, m.p. 243°. (Found : N, 15·96. $C_{17}H_{14}O_3N_4S$ requires N, 15·81 per cent.).

5-*Styryl*-2-p-*toluidino*-1 : 3 : 4-*thiodiazole*.—It was obtained by oxidising cinnamylidene-4-*p*-tolyl-thiosemicarbazone. The wate insoluble product was crystallised from acetic acid in light yellow rectangles, m.p. 184°. (Found : N, 14·16. $C_{17}H_{15}N_3S$ requires N, 14·34 per cent.).

5-*Phenyl*-2-*allylamino*-1 : 3 : 4-*thiodiazole*.—It was prepared by oxidising benzylidene-4-allylthiosemicarbazone. The oily product formed which was insoluble in water was then treated with steam and allowed to stand overnight when it solidified to a crystalline mass. This was crystallised from alcohol in white plates, m.p. 114°-115°. (Found : N, 19·35. $C_{11}H_{11}N_3S$ requires N, 19·25 per cent.).

Acetyl derivative.—Prepared in the usual way and crystallised from acetic acid in white rectangles it melts at 120°. (Found : N, 16·35. $C_{13}H_{13}ON_3S$ requires N, 16·21 per cent.).

5-m-*Nitrophenyl*-2-*allylamino*-1 : 3 : 4-*thiodiazole*.—On heating the *m*-nitrobenzylidene-4-allylthiosemicarbazone with the oxidising agent in alcoholic solution for 15 mins. and cooling the solution, the thiodiazole separated out. Crystallised from alcohol in white prisms with a faint yellow tinge it melts at 170°-171°. (Found : N, 21·58. $C_{11}H_{10}O_2N_4S$ requires N, 21·37 per cent.).

5-p-*Nitrophenyl*-2-m-*toluidino*-1 : 3 : 4-*thiodiazole*.—The separated solid obtained from the oxidation of *p*-nitrobenzylidene-4-*m*-tolyl

thiosemicarbazone (m.p. 192°) was crystallised from acetic acid in deep yellow plates, m.p. 257°. (Found: N, 18·21. $C_{15}H_{12}O_2N_4S$ requires N, 17·94 per cent.).

5-*Phenyl*-2-m-*toluidino*-1:3:4-*thiodiazole*.—The oily resinous mass obtained by oxidising benzylidene-4-*m*-tolyl-thiosemicarbazone (m.p. 160°) was subjected to steam distillation and cooled; the solid mass obtained was dissolved in alcohol, boiled with animal charcoal and filtered. On cooling crystals appeared which were recrystallised from benzene in white plates, m.p 176°. (Found: 16·62 $C_{15}H_{13}N_3S$ requires N, 15·73 per cent.).

5-m-*Nitrophenyl*-2-o-*toluidino*-1:3:4-*thiodiazole*.—It was prepared by oxidising *m*-nitrobenzylidene-4-*o*-tolylthiosemicarbazone (m.p. 219°) and crystallised from pyridine in light yellow needles, m.p. 247°-248°. (Found: N, 17·82. $C_{15}H_{11}O_2N_4S$ requires N, 17·94 per cent.).

5 m-*Nitrophenyl*-2-*methylamino*-1:3:4-*thiodiazole*.—Prepared from *m*-nitrobenzylidene-4-methylthiosemicarbazone. Crystals which separated from the aqueous solution on cooling were crystallised from alcohol in yellow needles, m.p. 201°. (Found: N, 23·85. $C_9H_8O_2N_4S$ requires N, 23·72 per cent.).

Acetyl derivative.—Obtained by heating the thiodiazole with acetic anhydride for 15 mins. and crystallised from pyridine in white plates, m.p. 225°-226°. (Found: N, 20·14. $C_{11}H_{10}O_3N_4S$ requires N, 20·14 per cent.).

Methyl derivative.—It was prepared by heating the above thiodiazole with methyl iodide in a sealed tube at 100° for three hours. On cooling crystals of the product separated which were crystallised from acetic acid in yellow plates, m.p. 209°. (Found: N, 22·52. $C_{10}H_{10}O_2N_4S$ requires N, 22·40 per cent.).

5-p-*Nitrophenyl*-2-*methylamino*-1:3:4-*thiodiazole*.—By oxidising *p*-nitrobenzylidene-4-methylthiosemicarbazone (m. p. 235°) the thiodiazole was obtained as a solid mass insoluble in water. Crystallised from pyridine it forms yellow needles, m.p. 262°. (Found: N, 23·83. $C_9H_8O_2N_4S$ requires N, 23·72 per cent.).

Its *acetyl derivative* was obtained in the usual way and crystallised from pyridine in white plates, m. p. 279°. (Found: S, 11·6%, $C_{11}H_{10}O_3N_4S$ requires S, 11·51 per cent.).

Its *methyl derivative* was prepared by heating the thiodiazole with methyl iodide as before. Crystallised from acetic acid in brown needles it melts at 203°. (Found: N, 22·37. $C_{10}H_{10}O_2N_4S$ requires N, 22·40 per cent.).

5-o-*Nitrophenyl*-2-m-*xylidino*-1 : 3 : 4-*thiodiazole*.—It was prepared from *o*-nitrobenzylidene-4-*m*-xylylthiosemicarbazone as before. The solid mass obtained was crystallised from acetic acid in pale yellow cubes, m. p. 229°. (Found: N, 17·23. $C_{16}H_{14}O_2N_4S$ requires N, 17·17 per cent.).

5-m-*Nitrophenyl*-2-m-*xylidino*-1 : 3 : 4-*thiodiazole*.—Obtained from the oxidation of *m*-nitrobenzylidene-4-*m*-xylylthiosemicarbazone (m. p. 232°) and crystallised from acetic acid it separates in light yellow plates, m. p. 205°. (Found: S, 10·29. $C_{16}H_{14}O_2N_4S$ requires S, 9·81 per cent.).

Its *acetyl derivative* prepared in the usual way was crystallised from alcohol in white needles, m. p. 197°-198°. (Found: N, 15·33. $C_{18}H_{16}O_3N_4S$ requires N, 15·21 per cent.).

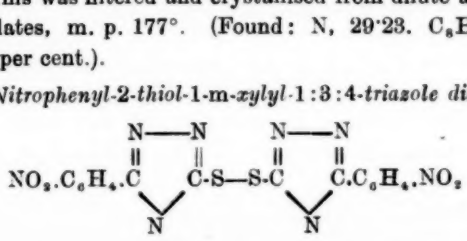
5-o-*Nitrophenyl*-2-*β*-*naphthylamino*-1 : 3 : 4-*thiodiazole*.—It was prepared from *o*-nitrobenzylidene-4-*β*-naphthyl-thiosemicarbazone (m. p. 213°) and crystallised from acetic acid in pale yellow plates, m. p. 202°. (Found: N, 16·18. $C_{18}H_{12}O_2N_4S$ requires N, 16·07 per cent.).

5-*Phenyl*-2-*ethylamino*-1 : 3 : 4-*thiodiazole*.—Obtained by oxidising benzylidene-4-ethylthiosemicarbazone and crystallised from acetic acid it separates in white plates, m. p. 238°-240°. (Found: N, 20·67. $C_{10}H_{11}N_3S$ requires N, 20·48 per cent.).

Oxidation of Thiosemicarbazones with Hydrogen Peroxide.

5-*Phenyl*-1 : 3 : 4-*triazole*.—The benzylidene-thiosemicarbazone was dissolved in alcohol and to the cooled solution hydrogen peroxide in excess was slowly added with frequent shaking. The reaction began at once with great evolution of heat and separation of sulphur. The mixture was then heated on a water-bath for 5 mins. to complete the reaction. The solution was filtered from sulphur and concentrated; the filtrate on cooling deposited a crystalline mass. This was filtered and crystallised from dilute alcohol in light yellow plates, m. p. 177°. (Found: N, 29·23. $C_8H_7N_3$ requires N, 28·96 per cent.).

5-o-*Nitrophenyl*-2-*thiol*-1-m-*xylyl*-1 : 3 : 4-*triazole disulphide*.



$C_6H_3(CH_3)_2$ $C_6H_3(CH_3)_2$

The *o*-nitrobenzylidene-4-*m*-xylylthiosemicarbazone was suspended in alcohol and oxidised as before with the required quantity of peroxide. The cold solution was filtered from the separated solid product, the residue washed with alcohol and crystallised from acetic acid in pale yellow plates, m. p. 201°-203°. (Found: N, 17·12, $C_{32}H_{36}O_4N_8S_4$ requires N, 17·23 per cent.).

5-Phenyl-2-thiol-1-allyl-1:3:4-triazole disulphide.—The benzylidene-4 allylthiosemicarbazone was oxidised as before. The separated solid was crystallised from acetic acid in yellow plates, m. p. 90°. (Found: N, 19·63. $C_{22}H_{20}N_6S_4$ requires N, 19·44 per cent.).

5-m-*Nitrophenyl-1-allyl-1:3:4-triazole.*—It was prepared either by oxidising the *m*-nitrobenzylidene-4-allylthiosemicarbazone with excess of peroxide or by oxidising the triazole disulphide with the same reagent. The product so obtained was crystallised from acetic acid in yellow plates, m. p. 194°-195°. (Found: N, 24·51. $C_{11}H_{10}O_2N_4$ requires N, 24·35 per cent.).

5-Phenyl-1-p-tolyl-2-thiol-1:3:4-triazole disulphide.—Benzylidene-4-*p*-tolylthiosemicarbazone was suspended in water and the oxidising agent added with shaking. On heating the mixture a vigorous reaction began with frothing. The mixture was heated for 20 mins., cooled and filtered. Crystallised from alcohol in pale yellow rectangles it melts at 155°-156°. (Found: S, 12·39. $C_{30}H_{24}N_6S_4$ requires S, 12·03 per cent.).

5-Phenyl-1-ethyl-2-thiol-1:3:4-triazole disulphide.—It was obtained from benzylidene-4-ethylthiosemicarbazone (m. p. 138°) in alcoholic suspension. The carbazone gradually went into solution on heating. From the clear solution on cooling the disulphide separated in yellow crystals, m. p. 88°. (Found: N, 20·89. $C_{20}H_{20}N_6S_4$ requires N, 20·59 per cent.).

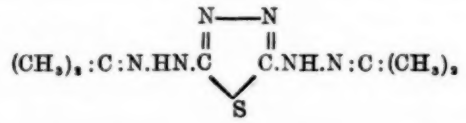
1: *5-Diphenyl-2-thiol-1:3:4-triazole disulphide.*—It was obtained from benzylidene-4-phenylthiosemicarbazone by oxidation as before. On heating the carbazone gradually dissolved and after heating for about 10 mins. the solution was cooled when the disulphide separated as a crystalline product. This was crystallised from acetic acid in white needles. It shrinks at 186° and melts at 232° with decomposition. (Found: N, 16·82. $C_{28}H_{20}N_6S_4$ requires N, 16·66 per cent.).

5-m-Nitrophenyl-2-thiol-1-allyl-1:3:4-triazole disulphide.—The *m*-nitrobenzylidene-4-allylthiosemicarbazone was oxidised in alcoholic suspension. The mixture was heated under reflux when the

reaction commenced with effervescence and the carbazone went into solution and after a few minutes the oxidation product separated as a crystalline solid. This was filtered and crystallised from acetic acid in yellow plates. It shrinks at 144° and melts at 173°. (Found: N, 21·28. $C_{13}H_{18}O_4N_6S_2$ requires N, 21·46 per cent.).

Oxidation of Acetone Thiosemicarbazones with Hydrogen Peroxide.

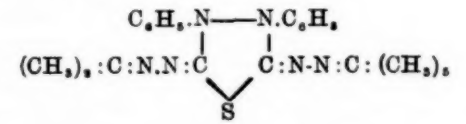
2: 5-*Diacetonehydrazido*-1: 3: 4-*thiodiazole*



The acetone-thiosemicarbazone was dissolved in alcohol and hydrogen peroxide was slowly added. The reaction began at once with evolution of heat. The solution was filtered from sulphur that separated out after heating the mixture for about 10 mins. and the crystals obtained on cooling the filtrate were recrystallised from alcohol in white rectangles, m. p. 260° with decomposition. (Found: S, 14·65. $C_8H_{14}N_6S$ requires S, 14·16 per cent.).

Heated with strong hydrochloric acid the above thiodiazole gradually dissolved after about one hour. The solution was filtered and concentrated; on cooling crystals of a hydrochloride separated, m. p. 157° with decomposition, which on analysis was found to be hydrazine hydrochloride.

2:5-*Diacetonehydrazide*-3:4-*diphenyl*-1:3:4-*thiodiazole*.



Acetone-4-phenylthiosemicarbazone (m. p. 125°) was covered with alcohol and the peroxide was slowly added, the mixture being cooled in ice water during addition. The reaction began immediately and the solid went into solution and after a few seconds a red crystalline product separated. This was filtered and crystallised from alcohol in golden yellow plates, m. p. 168° with decomposition. (Found: N, 22·13. $C_{30}H_{32}N_6S$ requires N, 22·13 per cent.).

The thiodiazole was decomposed by heating with strong hydrochloric acid. The solution was filtered, concentrated and from the solution hydrazine hydrochloride separated out.

2:5-*Diacetonehydrazido*-3:4-*di*-p-*tolyl*-1:3:4-*thiodiazole*.

Acetone-4-*p*-tolylthiosemicarbazone (m. p. 139°) was oxidised as before in aqueous suspension. On heating the mixture an oily substance separated which solidified after cooling. Crystallised from methyl alcohol with the addition of animal charcoal it separates in red prisms, m. p. 124°. (Found: N, 20·81. $C_{11}H_{10}N_6S$ requires N, 20·69 per cent.).

Our best thanks are due to Prof. J. C. Ghosh, D.Sc., and Dr. P. C. Guha for their kind interest and encouragement during the progress of this investigation.

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A New Method of Inversion of Geometrical Isomers by an Exothermic Reaction: Conversion of Maleic into Fumaric Acid.

By P. Neogi, Sukumar Neogi and Manas Prasun Chatterji.

The mutual conversion of geometrical isomers or geometrical inversion has been effected both by physical and chemical agencies. Transformation of this character was first observed with fumaric and maleic acids and later on with citraconic and mesaconic, oleic and elaidic, angelic and tiglic, cinnamic and *allo*cinnamic acids and other geometrical isomers. Physical agencies such as sunlight (Paal and Schulze, *Ber.*, 1902, **35**, 168), heat (Tanatar, *Ber.*, 1894, **27**, 1365), etc., and chemical reagents, specially small amounts of halogens (Wislicenus, *Ber.*, 1895, **28**, 1080 2693) or halogen hydracids, as a rule, transform the labile isomer into the stable one. Ultraviolet light (Stoermer, *Ber.*, 1009, **42**, 4865 and subsequent papers) also is known to effect inversion of the stable into the labile modification.

The exact mechanism of the transformation has not yet been definitely established. It was Wislicenus ("Raumliche Anordnung der Atome," Leipzig, 1889) who first tried to solve the problem. He explained the inversion brought about by chemical agents by assuming that the agent at first formed an additive derivative with one of the isomers and was subsequently removed. But later on this view has been shown to be untenable by Anschutz, Fittig, Michael and Skraup (*Monatsh*, 1891, **12**, 108).

Later on Skraup has shown most strikingly (*Monatsh.*, 1891, **12**, 107 and subsequent papers) that neither sulphur dioxide nor hydrogen sulphide alone is able to transform maleic into fumaric acid but that a mixture of the two will bring about the transformation. Based on this experimental result, Skraup suggests that an exothermic reaction such as the combined action of sulphur dioxide and hydrogen sulphide in a solution of the isomer acts catalytically in setting up vibrations which he compares to the physical phenomenon of resonance or the chemical effect of an explosion wave, or in other words the chemical reaction between the hydrogen sulphide and sulphur dioxide may be regarded as a type of detonator which starts the transformation in the maleic acid.

Up till now no further experimental work in support of Skraup's theory had been advanced. The present paper adds further experimental support to Skraup's work. Whilst searching for different exothermal reactions which would cause inversions we have found that neither sulphur dioxide nor manganese dioxide can alone transform maleic acid into its geometrical isomer, but when sulphur dioxide is passed into a solution of maleic acid in which finely divided manganese dioxide is suspended the conversion of maleic into fumaric acid takes place most readily in a few minutes. This would be a very interesting addition to the solitary case of the interaction of sulphur dioxide and sulphuretted hydrogen causing inversion as discovered by Skraup.

Experimental.

Maleic acid (1·5 g.) was dissolved in water (5 c. c.) and taken in a long hard glass test tube and purified sulphur dioxide was passed into the solution for more than an hour. No precipitate separated and on evaporating in a vacuum desiccator the residue left was entirely maleic acid (m. p. 130°). Therefore no inversion took place.

The same experiment was performed with manganese dioxide instead of sulphur dioxide at the ordinary temperature and it was found that no inversion took place.

1·5 Gm. of maleic acid were then dissolved in 5 c. c. of water in a long hard glass test tube. 2 Gm. of manganese dioxide well pulverised in a mortar were suspended in the aqueous solution of maleic acid and sulphur dioxide was passed into it. Gradually the temperature of the solution rose from 27° (room temparature) to 60°. The gas was passed for about *five minutes*. Gradually a white precipitate was thrown out of the solution. By this time almost the whole of the manganese dioxide went into solution. Then the white precipitate together with a little undecomposed manganese dioxide was filtered off, washed with a little water to remove any adhering maleic acid and manganous salts and treated with absolute alcohol which dissolved the fumaric acid leaving manganese dioxide behind. The alcoholic solution was filtered and then evaporated in a vacuum desiccator. The crystals that separated were washed with carbon disulphide, collected and identified to be those of fumaric acid. The substance was insoluble in water and sublimed

at 200°. The ethyl ester of the acid obtained was prepared and its boiling point was found to be 218° which is the same as that of ethyl fumerate. About 50 % of the maleic acid underwent inversion.

It is to be noted that the precipitation of fumaric acid was complete within five minutes. If, however, sulphur dioxide was passed for a longer period the precipitate of fumaric acid disappeared and various sorts of manganese were obtained in the solution.

With a view to ascertain the effect of temperature the same experiment with manganese dioxide and sulphur dioxide was carried out in an exactly similar manner, the temperature of the reacting medium however being lowered down to 15° and maintained at that temperature by surrounding the reaction tube with ice water. This time only a 10 % inversion was observed. When on the other hand the temperature of the reacting medium was maintained near about 90°, the percentage of transformation was still 50.[1] This is probably due to an equilibrium being set up between the two isomers.

1·5 Gm. of maleic acid were dissolved in 5 c. c. of absolute alcohol and 2 Gm. of pulverised manganese dioxide were suspended in the solution and sulphur dioxide was passed into it. The sulphur dioxide did not react with manganese dioxide in the alcoholic solution and no heat was evolved. No inversion was observed owing to the absence of any reaction. If, however, the alcohol was diluted with an equal volume of water and then sulphur dioxide was passed, it reacted with manganese dioxide and maleic acid was partially converted into fumaric acid.

The same experiment was carried out with an ethereal solution of maleic acid. There was no reaction between manganese dioxide and sulphur dioxide and no inversion was observed.

With a view to ascertain the effect of the reaction between sulphur dioxide and peroxides other than manganese dioxide, 1·5 Gm. of maleic acid were dissolved in 5 c. c. of water and the manganese dioxide was replaced by powdered lead peroxide, and sulphur dioxide was passed into the solution for more than an hour. There was scarcely any reaction and evolution of heat, and no fumaric acid was found to separate.

Similar negative results were obtained by using barium peroxide.

[1] Blank experiments showed that aqueous solutions of maleic acid do not yield fumaric acid even when evaporated to dryness on a water-bath.

In order to ascertain if the inversion was being effected by the heat of the reaction alone, the effect of the action of water on phosphorus pentoxide in which a very large amount of heat is evolved, was next tried. 1·5 Gm. of maleic acid were dissolved in 5 c.c. of water and taken in a basin and a small quantity of phosphorus pentoxide was sprinkled on the solution. Phosphorus pentoxide went into solution with the evolution of a considerable amount of heat and the temperature of the solution rose to about 60°. It was then cooled. No separation of fumaric acid took place even when the solution was cooled.

The last point that was elucidated was to ascertain if the products, *viz.*, manganese dithionate and manganous sulphate obtained by the interaction of manganese dioxide and sulpher dioxide were the real agents which produced inversion. It will be observed from the following experiments that the reaction products do not cause inversion.

1 Gm. of finely powdered manganese dioxide was suspended in 5 c.c. of water and sulphur dioxide was passed through it for 20 minutes. It was then filtered and the filtrate was poured into an aqueous solution of maleic acid (3 c.c. of water containing 1·5 Gm. of maleic acid). The temperature of the solution was kept at 30° for 5 minutes and no fumaric acid separated from the solution. The maleic acid was recovered unchanged on evaporating the solution in a vacuum desiccator and extraction with alcohol.

In order to ascertain if the reaction product would produce inversion at an elevated temperature, the above experiment was carried out in an exactly similar manner, the temperature of the reacting medium however being raised to 60° and maintained at that temperature for 5 minutes. No fumaric acid was formed, and as before maleic acid was recovered unchanged.

Discussion.

From the foregoing experiments it would be observed that the following facts have been established:—

(1) Neither sulphur dioxide nor manganese dioxide alone can effect the transformation.

(2) When sulphur dioxide is passed into a solution of maleic acid in water in which finely divided manganese dioxide was suspended, conversion of maleic into fumaric acid took place in a few minutes. About 50% transformation took place in 2 or 3 minutes. The mere

presence of the reaction acted catalytically in bringing about the transformation.

(3) When the temperature was maintained at 15° a 10% transformation was observed. On the other hand when the temperature of the reacting medium was maintained at about 90° the inversion was still 50%. Probably an equilibrium had been set up between the two isomers.

(4) Inversion did not take place in ether or alcoholic medium. When however the alcoholic solution was replaced by an aqueous-alcoholic one, partial conversion took place.

(5) Inversion did not take place when manganese dioxide was replaced by barium peroxide or lead peroxide.

(6) No inversion was observed when phosphorous pentoxide was added to an aqueous solution of maleic acid. This conclusively proves that the evolution of heat of a reaction is not the agency to produce inversion but the nature of the reaction plays an important part in the phenomenon.

(7) Inversion does not take place if the *resultant products of the reaction* between sulphur dioxide and manganese dioxide are added to an aqueous solution of maleic acid under the same conditions showing that inversion takes place in the midst of the reaction itself.

The foregoing experimental evidences, *viz.*, that neither sulphur dioxide nor manganese dioxide alone can bring about the transformation of maleic into fumaric acid but that inversion starts immediately when the reaction between sulphur dioxide and manganese dioxide is allowed to go on in the solution of the labile isomer would lend support to the " vibration theory " as postulated by Skraup. It would, however, be safer merely to note that the presence of an exothermic reaction like the one studied in this work, though not in general, might act catalytically in starting the transformation, or in other words this would be another instance of a chemical reaction catalytically influencing inversion in the place of a single catalytic substance like bromine or a halogen acid. Further work on this subject with other geometrical isomers is in progress.

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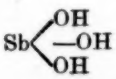
Organo-antimony Compounds. Part II. The Constitution of *p*-Aminostibinic Acid and its Amine Salts.

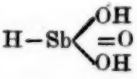
By Sudhir Chandra Niyogy.

The preparation of aromatic antimonials is now invariably carried out by the replacement of a diazo complex by antimonious acid in a suitable form and in an alkaline medium. In the event of the compound to be 'stibinated' containing a nitro group, the reaction medium is to be maintained almost neutral or even faintly acid to avoid undesirable side reactions (D.R.P. 254421). Previous attempts to stibinate aromatic compounds by the well known Beâchamp condensation were unsuccessful and the statement that aniline when heated with antimony trichloride gave rise to *p*-amino stibonous chloride (Breinl and Nierenstein, *Ann. Tropical Medicine & Parasit.*, 1908, **21**, 379) proved to be erroneous (May, "The Chemistry of Synthetic Drugs," p. 215). The only remaining source of the aryl stibinic acids (previous to the discovery of the diazo reaction mentioned above) was the triaryl stibines and its dihalides and by their careful and progressive dearylation, a number of derivatives of phenyl and *p*-tolyl series were obtained. This process of dearylation was frequently accompanied by changes in which the bond between carbon and anitmony was ruptured and the expected degradation product could not be isolated.

Although a number of patents has been taken out to cover the preparation of the various stibinic acids, the mechanism of the reaction does not appear to have been completely studied. Schmidt (*Annalen*, 1920, **421**, 174) suggested that antimony oxide in order to take part in the reaction, must be in its hydrated form *i.e.*, as antimonious acid, which is capable of existence in tautomeric forms represented by the following:—

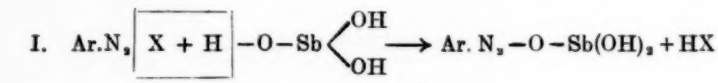


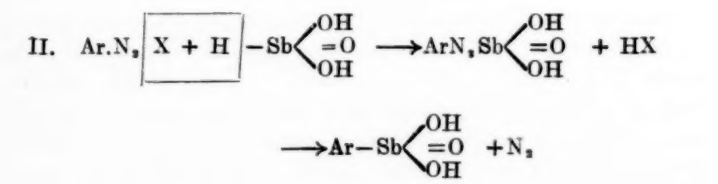
(1)



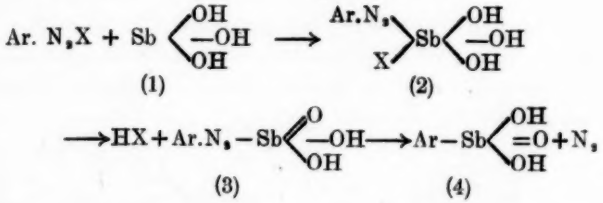
(2)

In the first, antimony is trivalent and in the second pentavalent. The reaction, according to D.R.P. 254421, takes place between the diazo salts and antimonious acids. If it is assumed that a molecule of HX is eliminated in the first stage forming a diazo-antimonial, which subsequently loses nitrogen, the course of the reaction may be represented as follows:—



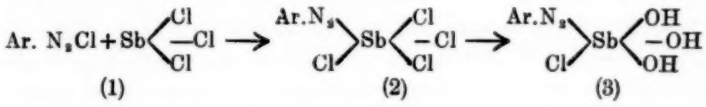


A compound of the type of Ar-O-Sb(OH)$_2$ which would be expected according to the first scheme, would be an aryl ester of antimonious acid and as such extremely unstable and would be at once hydrolysed into phenol and antimonious acid (Mackey, *J. Chem. Soc.*, 1909, **95**, 604). So it is necessary to assume that antimony oxide reacts in the pentavalent form, if there is an elimination of HX in the first stage. But the reaction can also be looked upon from another standpoint. Trivalent antimony compounds always exhibit a great tendency to pass to pentavalent forms. The action therefore can very easily be explained as follows:—

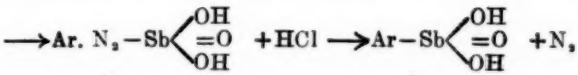


To settle this question it is necessary to study another series of reactions. May (*J. Chem. Soc.*, 1912, **101**, 1037) during his study

of the action of diazonium chlorides on antimony trichlorides noticed that these two substances in acid solution gave rise to stable crystalline insoluble additive compounds, which can be kept in the dry state without any risk of explosion. It is possible to arrive at a definite conclusion as to whether the antimony reacts in the trivalent or pentavalent form, from a study of these additive compounds:—



(1) (2) (3)



(4) (5)

It thus appears that the probability of the antimony reacting in the trivalent form is greater than that of its reacting in the pentavalent condition.

The yield of aryl stibinic acid prepared by the diazo reaction leaves much to be desired. It is found that during the process of the elimination of nitrogen, dark coloured bye-products and reduction products are always obtained. The latter consists of a compound in which the diazo complex has been replaced by hydrogen. With careful regulation of the reaction this can be controlled to a considerable extent. It is well known that the replacement of a diazo-group takes place through the *syn*-diazo form while its reduction involves the *anti*-configuration. Since the conversion of *syn*- to *anti*-configuration is markedly influenced by the alkalinity of the reaction medium, it is of the utmost importance that this should be carefully regulated, if the reduction process is to be kept to a minimum. In general, in applying this reaction, the reaction medium may be kept more alkaline than in the case of the corresponding arsenicals.

The nature of the aryl stibinic acid is a matter of controversy. Schmidt (*Ber.*, 1922, **55**, 697) maintains that they are complex in character as in the following $(ArSbO_3H_2)_3$ which may also be written as $\{(3\ ArSbO_3)H_2O\}2H_2O$ because it is found that two molecules of water can be easily removed in a vacuum desiccator while the remaining molecule is very firmly attached to the molecule. In their behaviour towards alkali, aryl stibinic acids

show some peculiarities, from which Schmidt (*loc. cit.*) concludes that they are complex in character. Macallum (*J. Soc. Chem. Ind.*, 1923, **42**, 468T) on the other hand, as the result of molecular weight determinations by the cryoscopic method, has come to the conclusion that they are simple molecules, $ArSbO_3H_2$. Turning now to the salts of the aryl stibinic acid, it is found that the nature of alkali used for preparing them, plays an important part. According to Schmidt (*loc. cit.*) sodium and potassium hydroxides finally bring about the dissociation of the complex molecules into its simplest form but with lithium hydroxide two molecules of the stibinic acid remain associated together even after complete neutralisation. The complex nature of the acids is also supported by the analysis of the alkali salts. Farghar and Gray (*J. Pharm. & Expt. Therap.*, 1921, **18**, 353) have found that in all samples analysed by them, the atomic ratio of alkali metal to antimony is almost 1:3. Dunning and Reid, however, have found in a recent work (*J. Amer. Chem. Soc.*, 1926, **48**, 2959; 1927, **49**, 2869) that some azo derivatives of *p*-aminophenyl stibinic acid gave the disodium salts.

This result is rather remarkable, when it is remembered that no previous worker had been able to prepare salts in which the atomic ratio of sodium to antimony is 2:1. The present work was undertaken to settle this question finally. It has been found that aryl stibinic acids are capable of forming salts with primary, secondary, and tertiary amines. These amines are certainly weaker than sodium or potassium hydroxide, so that the dissociation of the complex molecule will not take place. Finally molecular weight determination of these amine salts ought to settle the question once for all. But unfortunately, the latter portion of the work could not be carried out as the amine salts form a clear solution in water which, however, gives rise to a white precipitate on standing. The analytical results obtained show that in every case there are 3 molecules of the stibinic acid to one molecule of the base, thus supporting Schmidt's contention.

The preparation of the starting material, *p*-aminophenyl stibinic acid, has been described by various workers (U. S. P. 1260707, D.R.P. 254121, E.P. 10350 (1912); and also Dunning and Reid, *J. Amer. Chem. Soc.*, 1926, **48**, 2959; 1927, **49**, 2869). But an unexpected result was obtained in the course of this work. The usual process consists of two stages:—(1) Treating a diazotised solution

of acetyl *p*-phenylene diamine with antimony trichloride in hydrochloric acid solution to obtain an additive compound and the decomposition of the same with dilute caustic soda to obtain 4-acetylaminophenyl stibinic acid; (2) hydrolysis of acetyl group with caustic soda solution. In one experiment, the additive compound described above was left to dry in a vacuum desiccator over soda-lime, as the mass was very slightly acid. On subsequent treatment with caustic soda solution it was found that the product was not 4-acetylaminophenyl stibinic acid but 4-aminophenyl stibinic acid. The alkaline hydrolysis of the acetyl group takes considerable time for completion and thus a great speeding up of the reaction is possible by leaving the faintly acid additive compound in a desiccator.

For the preparation of the amine salts it was found essential that the 4-aminophenyl stibinic acid should be in the highest state of purity attainable. Repeated washing with distilled water failed to effect the complete purification. The crude acid was converted into the hydrochloride of the stibinic chloride $SbCl_4 . C_6H_4 . NH_2 . HCl$ by treatment with concentrated hydrochloric acid. When decomposed with the calculated quantity of caustic soda, the chloride yielded the free acid, which after repeated washing, was in a sufficiently pure state for the next operation. The purified acid was then suspended in water and an aqueous or alcoholic solution of the base was added drop by drop, till the whole went into solution. The solution was then heated on a water-bath for some time, filtered from any precipitates and rectified spirit was added in excess when the salt separated out.

Experimental.

Preparation of p-Aminophenyl Stibinic Acid.—Acetyl *p*-phenylene diamine (100 g.) was added to water (300 c.c.) and hydrochloric acid (37%, 100 c.c.). A portion of the hydrochloride separated out. The whole was then cooled to 0° with crushed ice and diazotised with a solution of sodium nitrite (50 g.). After diazotisation, hydrochloric acid (50 c.c.) was further added. To this solution was gradually added, with stirring, a solution of antimony trichloride prepared by dissolving antimony trioxide (70 g.) in hydrochloric acid (250 c.c.). An almost colourless crystalline precipitate, immediately separated which was filtered, washed first with dilute hydrochloric acid and

then with water to remove hydrochloric acid. It was found that the wash water was very slightly acid. The moist mass was then left to dry in a vacuum desiccator over soda-lime for 48 hours. When opened, it was found that the mass was still somewhat moist: yield—250 g.

25 Gm. of the moist mass was beaten up with water (100-125 c.c.) and cooled with cracked ice to 0-5°. Caustic soda solution (8 gm.) in 50-60 c.c. of water was gradually added with vigorous stirring. The evolution of nitrogen ceased in about 30 minutes. The alkaline solution was then almost neutralised with dilute sulphuric acid, saturated with carbon dioxide for 30 minutes and filtered. The clear filtrate, on acidifying with dilute acetic acid, gave a colourless gelatinous precipitate which was found to be soluble in dilute mineral acids. The solution in mineral acids also gave the usual diazo reaction. Thus it was concluded that the precipitate was not 4-acetylaminophenyl stibinic acid but 4-aminophenyl stibinic acid. The precipitated stibinic acid was then filtered, washed repeatedly with distilled water to remove inorganic impurities and then dissolved in conc. hydrochloric acid and precipitated with the required quantity of caustic soda solution. This was again filtered off washed with distilled water and suspended in water. As 4-aminophenyl stibinic acid decomposes very easily in the dry state, it cannot be preserved in a dry condition and should always be kept suspended in water or as its alkali salt.

To the suspension of 4-aminophenyl stibinic acid in water, was gradually added a solution of methylamine in water, till the whole went into solution. The clear red solution was then heated on a water-bath for about 5 minutes A gelatinous precipitate generally separates which was filtered off and to the clear filtrate a large excess of rectified spirit was added. A white or very slightly coloured precipitate separated which was allowed to stand overnight, filtered, washed with rectified spirit and then with absolute alcohol and dried in a vacuum desiccator over fused calcium chloride. (Found: C, 27·48; H, 3·23; Sb, 45·1. $(NH_2C_6H_4SbO_3H_2)_3CH_3.NH_2$ requires C, 28·04; H, 3·5; Sb, 44·2 per cent.).

The preparation of the other salts was carried out in exactly the same way, taking care not to heat the solution of the stibinic acid above 80° or for a long time.

Dimethylamine Salt.—(Found: C, 27·8; H, 4·4; Sb, 43·4. $(NH_2C_6H_4SbO_3H_2)_2NH(CH_3)_2$ requires C, 28·8, H, 3·7, Sb, 43·1 per cent.).

Trimethylamine Salt.—(Found: C, 29·1; H, 3·02; Sb, 42·9. $(NH_2C_6H_4SbO_3H_2)_3N(CH_3)_3$ requires C, 29·8; H, 3·9; Sb, 42·6 per cent.).

Ethylamine Salt.—(Found: C, 27·6; H, 4·23; Sb, 42·8. $(NH_2C_6H_4SbO_3H_2)_3C_2H_5NH_2$ requires C, 28·8; H, 3·7; Sb, 43·4 per cent.)

Diethylamine Salt.—(Found: C, 29·8; H, 3·84; Sb, 41·9. $(NH_2C_6H_4SbO_3H_2)_3NH(C_2H_5)_2$ requires C, 30·7; H, 4·07; Sb, 42·6 per cent.)

Triethylamine Salt.—(Found: C, 33·21; H, 3·95; Sb, 39·4. $(NH_2C_6H_4SbO_3H_2)_3N(C_2H_5)_3$ requires C, 32·4; H, 4·4; Sb, 40·54 per cent.)

Propylamine Salt.—(Found: C, 29·1; H, 3·7; Sb, 43·2. $(NH_2C_6H_4SbO_3H_2)_3C_3H_7NH_2$ requires C, 29·8; H, 3·2; Sb, 42·6 per cent.)

iso*Amylamine Salt.*—(Found: C, 32·2; H, 4·38; Sb, 40·6. $(NH_2C_6H_4SbO_3H_2)_3C_5H_{11}NH_2$ requires C, 31·6; H, 3·84; Sb, 41·2 per cent.)

Allylamine Salt.—(Found: C, 29·07; H, 4·2; Sb, 42·3. $(NH_2C_6H_4SbO_3H_2)_3CH_2:CH.CH_2NH_2$ requires C, 29·88; H, 3·66; Sb, 42·7 per cent.)

Properties.—All these amine salts are almost colourless amorphous solids having no definite melting point. They dissolve freely in water forming a clear red solution which in a few minutes turns opaque due to the separation of a white precipitate. Moist air and atmospheric carbon dioxide cause some decomposition in them, as when thus exposed they are no longer soluble in water. They are insoluble in all organic solvents except glycerine, in which they dissolve on heating and can be precipitated by adding alcohol.

I desire to express my thanks to Prof. H. K. Sen, for the kind interest he has taken in this work and lso to Mr. Kshitish Chandra Bose-Ray for having helped me in the analytical portion of the work.

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Kinetic Salt Effect. Part I. The Reaction between Sodium Monochloracetate and Sodium Thiosulphate.

By A. N. Kappanna.

Brönsted's theory (*Zeit. physikal. Chem.*, 1922, **102**, 169) of reaction velocity in ionic reactions postulates the formation of a critical complex, the valency and activity of which form two very important determining factors, so far as the reaction velocity is concerned. The application of the theory has so far been limited to reactions taking place with measurable velocities at and in the neighbourhood of 25°, since at this temperature the activity coefficients of ions of different valence types are known pretty accurately. At higher temperatures we have at present practically no data regarding activity coefficients of ions even in dilute solutions. The experiments described in this paper were made with the object of observing how the kinetic activity coefficient of a reaction varies with total ionic concentration at higher temperatures. If we start with a reaction whose mechanism is well-known and study the variation in the velocity constant with total ionic concentration, we can calculate the variation in the kinetic activity coefficient at that temperature with reference to its value at a particular concentration (say 0·02N). This does not of course enable us to form a quantitative idea about the values of activity coefficients of individual ions, but when the variation of the kinetic activity coefficients with concentration of a number of reaction involving ions of different valence types are known at any given temperature, a relative idea regarding the variation of the activity coefficient of any ion with concentration could be formed.

The mechanism of the reaction between sodium chloracetate and sodium thiosulphate was studied by Slator (*J. Chem. Soc.*, 1905, **87**, 481) who found it to be a bimolecular reaction taking place with measurable velocities above 50° according to the following scheme, between the ions

$$CH_2ClCOO^- + S_2O_3^{--} \longrightarrow CH_2S_2O_3COO'' + Cl'$$

On the basis of Brönsted's theory, the critical complex would be $CH_2ClCOO.S_2O_3'''$. If f_1, f_2, and f_3 represent the activity coefficients

of uni-, bi- and tri-valent ions respectively at a given concentration the kinetic activity coefficient F would be equal to $f_1.f_2/f_3$ and

$$-\frac{dc}{dt}=h.C_{CH_2ClCOO'}.C_{S_2O_3''}.F.$$

where C stands for the concentrations of the reacting components and h, the velocity constant independent of the total ionic concentration. From the older form of equation,

$$-\frac{dc}{dt}=K.C_{CH_2ClCOO'}.C_{S_2O_3''}$$

we can determine the velocity constant K, at different concentrations and therefrom evaluate the variable F.

Experimental.

Velocity measurements were made at 50°, 60° and 70° with different concentrations of the reacting components. The reaction was followed as was done by Slator (*loc. cit.*) by titrating a known quantity of the reaction mixture with N/100 iodine solution. All the salts used in the work were carefully purified by recrystallisation. Tables I-III contain results of three experiments at 60° at different total concentrations. The bimolecular constants obtained are excellent. Ten c.c of the reaction mixture was titrated in each case.

Table I.

$CH_2ClCOONa$=0·10M. Temperature 60°.
$Na_2S_2O_3$=0·025M. 10 c.c titrated.

Time in min.	C.c. $Na_2S_2O_3$	C.c. $CH_2ClCOONa$	K
0	22·90	97·90	—
10	18·20	93·20	0·1044
20	14·60	89·60	0·1045
30	11·85	86·85	0·1040
40	9·65	84·65	0·1041
60	6·60	81·60	0·1030
8	0	75	—
		Mean ...	0·1040

TABLE II.

Sodium chloracetate=0·05M.
Sodium thiosulphate=0·025M. 10 c.c titrated.

Time in min.	C.c. $Na_2S_2O_3$	C.c. $CH_2ClCOONa$	K
0	23·85	48·85	—
10	21·45	46·45	0·0972
20	19·40	44·40	0·0965
30	17·60	42·60	0·0968
50	14·70	39·70	0·0960
70	12·40	37·40	0·0960
		Mean ...	0·0965

TABLE III.

Sodium chloracetate=0·02M.
Sodium thiosulphate=0·015M. 10 C.c. titrated.

Time in min.	C.c. $Na_2S_2O_3$	C.c. $CH_2ClCOONa$	K
0	14·30	19·30	—
20	13·30	18·30	0·0830
40	12·40	17·40	0·0840
60	11·65	16·65	0·0822
100	10·30	15·30	0·0832
200	7·85	12·85	0·0836
		Mean ...	0·0832

Table IV contains a summary of the data at 60°. Some experiments made with the addition of neutral salts are also included in the table.

TABLE IV.

Conc. $Na_2S_2O_3$	$CH_2ClCOONa$	Neutral salt	Total equiv. ionic conc.	K
0·025M	0·10M	...	0·15N	0·1040
0·025M	0·05M	0·05*M*KCl	0·15N	0·1045
0·025M	0·05M	...	0·10N	0·0965
0·020M	0·04M	0·02*N*.KCl	0·10N	0·0970
0·020M	0·04M	...	0·08N	0·0930
0·010M	0·05M	...	0·07N	0·0890
0·010M	0·02M	...	0·04N	0·0805
0·005M	0·01M	...	0·02N	0·0675

It is obvious from the figures given in the table that the velocity depends upon the total ionic concentration and the primary salt effect is positive. This is what is to be expected in a reaction that takes place between similarly charged ions.

Table V contains results of velocity measurements between 50° and 70°.

TABLE V.

Total equiv. ionic conc.	$K_{25}°$	$K_{50}°$	$K_{70}°$	$\frac{K_{50}°}{K_{25}°}$	$\frac{K_{70}°}{K_{50}°}$
0·02 N	0·034	0·0675	0·141	1·98	2·09
0·04 N	0·041	0·0805	0·161	1·96	1·99
0·08 N	0·046	0·0930	0·097	2·02	2·04
0·10 N	0·048	0·0970	0·202	2·02	2·08
0·15 N	0·051	0·1040	0·210	2·04	2·02

The temperature coefficients of the reaction at all concentrations on either side of 60° appear to be identical and equal to 2 within limits of experimental error.

Table VI gives the variation of the kinetic activity coefficient at different temperatures, assuming the factor F to have a value unity at 0·02N total ionic concentration. Values for 25° are included for comparison and are taken from Brönsted (*loc. cit.*).

TABLE VI.

Total equiv. ionic conc.	$F_{25}°$	$F_{50}°$	$F_{60}°$	$F_{70}°$
0·02 N	1	1	1	1
0·04 N	1·30	1·206	1·192	1·141
0·08 N	1·635	1·353	1·380	1·347
0·10 N	1·77	1·412	1·437	1·432
0·15N	—	1·500	1·540	1·489

The kinetic activity coefficients are very much the same at the three different temperatures for the same ionic concentrations but very much smaller as compared to their values at 25°. The only inference that could be drawn here is that perhaps the kinetic activity coefficient falls rapidly between 25° and 50° at any given

concentration and then remains practically constant with further increase in temperature.

Specific Ionic Action.—The effect of adding varying quantities of different neutral salts on the velocity of reaction was studied with the object of finding out if different ions at high concentrations exhibit any specific influences or whether as in the case of dilute solutions the velocity merely depends upon the total ionic concentration. The effects of the following salts has been tested KCl, NH_4Cl, NaCl, LiCl, K_2SO_4, $(NH_4)_2SO_4$, Na_2SO_4, KNO_3, $NaNO_3$, and NH_4NO_3. The reaction mixture in each case consisted of 0·10M sodium chloracetate and 0·025 M thiosulphate : to this different amounts of salts were added. All the experiments were carried out at 50°.

TABLE VII.

Salt.	*Velocity constants at different salt concentrations.*		
	0·50 N	1·0 N	2·0 N
KCl	0·0623	0·0745	0·0878
NH_4Cl	0·0618	0·0703	0·0821
NaCl	0·0600	0·0670	0·0767
LiCl	0·0553	0·0590	0·0686
KNO_3	0·0613	0·0728	0·0851
NH_4NO_3	0·0606	0·0690	0·0801
$NaNO_3$	0·0574	0·0644	0·0743
K_2SO_4	0·0591	0·0670	0·0778
$(NH_4)_2SO_4$	0·0590	0·0666	0·0761
Na_2SO_4	0·0570	0·0640	0·0733

Velocity constant with only the reacting components was 0·051.

Table VII gives the results. A study of the table reveals that some ions are more effective than certain others in increasing the velocity. Anions and cations shall be separately arranged in the following orders: $K > NH_4 > Na > Li > Cl > NO_3 > SO_4$.

Kiss and Bruckner (*Zeit. physikal. Chem.*, 1927, **128**, 71) have also found these ions to be effective in the same order in their study of the reaction between potassium persulphate and iodide ion. The only general relationship they were able to trace between the specific effect of the ion and its physical properties was that so

far as univalent cations were concerned the ions having a greater ionic volume had a greater accelerating effect. In the case of anions it is interesting to note that $Cl > NO_3 > SO_4$ is in the same order as the strengths of aqueous solutions of their acids $HCl > HNO_3 > H_2SO_4$. It is also to be noticed that at the concentrations of the salts given in Table VII the rate of increase of velocity with concentration is very small. The tendency is for the velocity to become almost constant at high concentrations. It is only in dilute solutions that the velocity may be said to vary almost linearly with total ionic concentration.

Summary.

Kinetics of the reaction between sodium monochloracetate and sodium thiosulphate have been studied between 50° and 70° at different concentrations.

With increasing total ionic concentration the velocity constant increases. This is in accordance with Brönsted's theory of reaction velocity in ionic reactions.

The temperature coefficient has been found to have the same value, 2, within narrow limits at different concentrations on either side of 60°.

The kinetic activity coefficient at the same ionic concentration does not appear to vary appreciably with increase in temperature between 50° and 70° although the fall between 25° and 50° appears to be very rapid.

The effect of ten neutral salts at high concentrations, ranging up to 2N, has been studied. The ions could be arranged in the following orders indicating their relative specific effects: $K > NH_4 > Na > Li$ and $Cl > NO_3 > SO_4$.

My best thanks are due to Prof. J. C. Ghosh for his kind interest in this work.

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On the Constitution of some Dinitro-*m*-cresols.

By Shrirang M. Sane and Shiam Sundar Joshi.

There are contradictory statements regarding the constitution of the dinitro-*m*-cresols. A dinitro-*m*-cresol having m.p. 74° is described by Gibbs and Robertson (*J. Chem. Soc.*, 1914, **105**, 1889) to which the authors assign the constitution 1-methyl-3-hydroxy-2:6-dinitrobenzene. The same authors also describe another dinitro-*m*-cresol having a m.p. 60° and to this they ascribe the constitution 1-methyl-3-hydroxy-4:6-dinitrobenzene. Will who prepared a large number of isomeric trinitrotoluenes obtained from one of these a dinitro-*m*-cresol of the constitution 1-methyl-3-hydroxy-4:6-dinitrobenzene having the melting point 74° (*Ber.*, 1914, **47**, 712). Borsche starting from 3-chloro-4:6-dinitrotoluene obtained, by replacement of the chlorine atom by hydroxyl group, 1-methyl-3-hydroxy-4:6-dinitrobenzene which melted at 63°—65° (*Ber.*, 1917, **50**, 1350).

From this brief summary it will be seen that two different dinitro-*m*-cresols are described in literature having the melting point 74°, while the dinitro-*m*-cresols described by Will and also by Borsche and having, according to these authors, the same constitution have different melting points.

In order to settle the constitution of these dinitro-*m*-cresols, the best method is to start from 3-chloro-4:6-dinitrotoluene the constitution of which has been proved beyond doubt (Reverdin and Crepieux, *Ber.*, 1900, **33**, 2506). We consequently repeated Borsche's experiment and found that the product obtained by fusing 3-chloro-4:6-dinitrotoluene with sodium acetate and acetamide does not melt at 63—65° but at 74°. That there is no migration of groups during this fusion is proved by the fact that the dinitrotoluidine obtained from the *p*-toluene sulphonyl ester of this dinitro-*m*-cresol is identical with the 3-amino-4:6-dinitrotoluene obtained by heating 3-chloro-4:6-dinitrotoluene with ammonia. This dinitrotoluidine is also identical with the dinitrotoluidine, (m.p. 194°) from which Will prepared his 4:6-dinitro-*m*-cresol (CH_3=1, OH=3). 1-Methyl-3-hydroxy-4:6-dinitrobenzene has therefore the melting point 74°.

The bromocompound obtained by the bromination of this dinitro-*m*-cresol has therefore the constitution 1-methyl-2-bromo-3-hydroxy-4:6-nitrobenzene (m.p. 115°—116°). The chloro-compound which we have obtained from the latter compound by the replacement of the hydroxyl group by chlorine has therefore the constitution: 1-methyl-2-bromo-3-chloro-4:6-dinitrobenzene (m.p. 81°—82°). This last compound is identical with the chlorobromodinitrotoluene which Cohen and Smithels (*J. Chem. Soc.*, 1914, **105**, 1909) obtained by nitrating 2:3-bromochlorotoluene. Gibbs and Robertson's 2:6-dinitro-*m*-cresol (m.p. 74°) is really 4:6-dinitro-*m*-cresol (OH=1, CH_3=3) and their and propably also Kehrmann's (*Annalen*, 1898, **303**, 29) 4-bromo-2:6-dinitro-*m*-cresol is 2-bromo-4:6-dinitro-*m*-cresol.

Experimental.

1-Methyl-3-hydroxy-4:6-dinitrobenzene was obtained from *m*-chlorotoluene as follows: A mixture of nitric acid (18 c.c.) and concentrated sulphuric acid (22 c.c.) was added gradually to *m*-chlorotoluene (12·6 g.). During nitration the mixture was cooled and well shaken and then left overnight. On adding water to this mixture 3-chloro-4:6-dinitrotoluene (18 g.) was obtained in pale white crystals, m.p. 91° (Reverdin and Crepieux, *Ber.*, 1900, **33**, 2505). Chlorodinitrotoluene (9·5 g.) was then heated with a mixture of anhydrous sodium acetate (9·5 g.) and acetamide (28·5 g.) for an hour at 180°. On treating the mass with water, dinitro-*m*-cresol was obtained (5·5 g.). It was recrystallised from acetic acid: yellow crystals, m.p. 74°. (Found: N, 14·08. $C_7H_6O_5N_2$ requires N, 14·14 per cent.)

*4:6-Dinitro-*m*-cresyl-*p*-toluene sulphonate* (OH=1, CH_3=3).—4:6-Dinitro-*m*-cresol (4 g.), *p*-toluenesulphonylchloride (4·2 g.) and diethylaniline (8 c.c.) were heated on water-bath for four hours. From the dark product diethylaniline was removed by means of hydrochloric acid. On rubbing the residue with alcohol, the dinitro-*m*-cresylsulphonate separated out in crystalline form (5·6 g.). It dissolves easily in acetone and benzene, but is not easily soluble in alcohol. Colourless crystals from alcohol; m.p. 110°—111°. (Found: S, 9·21. $C_{14}H_{12}O_7N_2S$ requires S, 9·11 per cent).

1-Methyl-3-amino-4:6-dinitrobenzene (4:6-dinitrotoluidine).—Through the boiling solution of 4:6-dinitro-*m*-cresylsulphonate (3·5 g.) in xylene, a current of dry ammonia was passed for about

an hour and xylene removed by means of steam. The residue was 4:6-dinitro-*m*-toludine (1·3 g.); yellow crystals from acetic acid, m.p. 194°. (Found: N, 21·14. $C_7H_7O_4N_3$ requires N, 21·31 per cent.).

1-*Methyl*-2-*bromo*-3-*hydroxy*-4:6-*dinitrobenzene* (2-Bromo-4:6-dinitro-*m* cresol: OH=1, CH_3=3).—This was obtained by adding bromine (1·1 c.c.) to a solution of 4:6-dinitro-*m*-cresol (4 g.) in acetic acid. On adding a little water to the mixture, the bromodinitrocresol separated out. It is easily soluble in alcohol and acetic acid. Orange yellow crystals from acetic acid; m.p. 115°—116°. (Found: Br, 29·09. $C_7H_5O_5N_2Br$ requires Br, 28·85 per cent.).

3-*Chloro*-2-*bromo*-4:6-*dinitrotoluene*.—A mixture of 2-bromo-4:6 dinitro-*m*-cresol (5·6 g.), *p*-toluenesulphonylchloride (4·2 g) and diethylaniline (12 c.c.) was heated on the water-bath for six hours. From the dark product the diethylaniline was removed by means of hydrochloric acid and the residue was shaken with sodium carbonate solution. The residue was then dissolved in alcohol and the solution boiled with animal charcoal. On concentrating the filtrate the chlorobromodinitrotoluene separated out. Easily soluble in most organic solvents; colourless crystals, m.p. 81°—82°. (Found: N, 9·19. $C_7H_4O_4N_2ClBr$ requires N, 9·48 per cent.).

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Relation between Hydration and Stability of Sols and the Bivalent Nature of Fluoride Ion.

By S. Ghosh and N. R. Dhar.

Colloids have been divided into two classes *viz.*, lyophile and lyophobe. There are, however, no definite criteria of distinguishing once class of the sol from the other. For example, gelatin, albumin, gum arabic, soap and saponin show much greater viscosity and markedly less surface tension than the dispersing medium, water. These sols are also highly stable towards electrolytes and readily form stiff jelly even in the diluted condition. These substances are typically lyophilic in nature and are considered to be highly solvated, but no direct experiments proving their great amount of hydration have yet been done. Though starch and agar agar have been classified as lyophile colloids they do not show marked decrease of surface tension but their other properties are the same as those of the first group of lyophile colloids.

We (*Z. anorg. Chem.*, 1926, **152**, 399 ; 1927, **164**, 63) have shown that sols of vanadium pentoxide and ceric hydroxide are more viscous than water and form stiff jellies even when dilute but they are unstable and readily coagulated by univalent electrolytes and their surface tension seems to be very slightly less than that of water. Hence it will be clear that it is difficult to state definitely the points of difference between lyophile and lyophobe colloids.

In communications (*Z. anorg. Chem.*, 1927, **162**, 237 ; **168**, 209 ; *Kolloid. Zeit.*, 1927, **42**, 120) from these laboratories we have shown that colloids can be divided into two classes according to their behaviour on ageing. In one class of sols the viscosity decreases and the surface tension and conductivity increase on ageing and this class appears to be less hydrated. The other class of sol becomes more viscous and less conducting and more hydrated on ageing. These latter class of sols are lyophilic in nature. If we classify the sols from the above criteria, hydroxides of iron, aluminium, chromium, tin, thorium, ceric (prepared in the hot), ferrocyanides of

iron and copper and arsenious sulphide and crystal violet show lyophobic behaviour, whilst vanadium pentoxide, ceric hydroxide (prepared in the cold) and gelatin have been found to possess lyophilic character.

It has been believed that there is a close relationship between the degree of hydration of a sol and its stability towards electrolytes. In a recent paper (*Kolloid.Zeit.*, 1928, **44**, 149) we have shown that the amount of electrolytes of different valencies required to coagulate the sols of ceric hydroxide, thorium hydroxide, ferric hydroxide and stannic hodroxide prepared in the cold and hot conditions are not very different from each other. The amount of hydration, however, is much greater with sols prepared in the cold than in the hot condition as is evident from their greater viscosities and the more gelatinous nature of the precipitates obtained with sols prepared in the cold than those in the hot. Thus we have obtained stable jellies with ceric hydroxide sol prepared in the cold whilst the sol prepared in the hot only forms a flocculent precipitate on coagulation. Similarly, we have observed that the precipitate from ferric hydroxide sol prepared in the hot is more granular than the precipitate obtained from the sol prepared in the cold. Hence it appears that greater hydration is not always associated with greater stability towards electrolytes.

In the same paper we have shown that the high coagulating power of fluoride ions observed with several positively charged sols is certainly due to their bivalent nature (F_2'') and not due to their greater degree of hydration than other halogen ions as has been assumed by Freundlich and Aschenbrenner (*Koll. Zeit.*, 1027, **41**, 37).

In this paper we have studied the coagulation of the hydroxides of zirconium, chromium and aluminium in order to strengthen our foregoing conclusions.

(1) *Zirconium hydroxide sol.*—This sol was prepared by (*a*) dialysing a zirconium nitrate solution and (*b*) boiling a zirconium nitrate solution and then dialysing the boiled solution. The first sol was the one prepared in the cold and the second sol was the one prepared in the hot. Both the sols form firm transparent jellies when coagulated by KCl, whilst only broken gelatinous precipitates are obtained when coagulated by bivalent or polyvalent anions. The following tables contain the results when zirconium hydroxide sol prepared in the cold and hot conditions are coagulated by different electrolytes.

TABLE I.

Coagulation of zirconium hydroxide sol prepared in the cold.

Concentration of the sol=9·42 gms. ZrO_2 per litre.
Amount of sol taken each time=2 c.c. Volume=4 c.c.
Time=1/2 hour.

Electrolytes.	Concentration.	Amount to gelatinise in c.c.	Precipitation value.
KCl	N/2	0·70	0·0875
KBr	N/2	0·80	0·1000
KI	N/2	0·90	0·1125
K_2SO_4	N/50	1·55	0·0078
K_2F_2	N/37·8	1·50	0·0106
$K_2C_2O_4$	N/50	1·90	0·0095
Sodium tartrate	N/50	2·2	0·0110
$K_4Fe(CN)_6$	N/500	1·25	0·0006

TABLE II.

Coagulation of zirconium hydroxide sol prepared in the hot.

Concentration of the sol=9·56 gms. ZrO_2 per litre.
Sol A= 2 c.c. of the sol made up to 4 c.c. Time=1 hour.

Electrolyte.		Precipitation value. Sol A.	Sol A/2.
KCl	N/4	0·0437	0·0437
KBr	N/4	0·0531	0·0500
KI	N/4	0·0812	0·0812
K_2SO_4	N/50	0·0070	0·0050
K_2F_2	N/37·8	0·0100	0·0070
$K_2C_2O_4$	N/50	0·0090	0·0065
Sodium tartrate	N/50	0·0095	0·0080
$K_4Fe(CN)_6$	N/500	0·0008	0·0004

Tables I and II show that the precipitation values of different

anions are in the following increasing order for both the sols:— ferrocyanide > sulphate > oxalate > tartrate > fluoride > chloride > bromide > iodide.

It will be also seen that zirconium hydroxide sol behaves normally towards dilution when coagulated by electrolytes. In the following tables the results are recorded when the sol prepared in the hot is coagulated with mixtures of KCl and K_2SO_4.

TABLE III.

Amount of sol taken each time=2 c.c.
Volume=4 c.c. Time=1/2 hour.

Amount of KCl added in c.c. N/4	Amount of K_2SO_4 required to coagulate in c.c. N/50.		
	Added.	Calculated.	Difference.
0·7	—	—	—
0	1·40	—	—
0·1	1·20	1·20	0
0·2	1·05	1·00	+0·05
0·3	0·80	0·80	0
0·4	0·62	0·60	+0·02

The above table shows that additive amounts of KCl and K_2SO_4 are required to coagulate the sol.

(2) *Chromium hydroxide sol.*—This sol was prepared in the cold by adding ammonium carbonate solution to a chromium chloride solution at the room temperature (25°) till a slight precipitate obtained just dissolved on shaking. The deep green coloured sol was left for dialysis till it was free from electrolytes. A portion of the sol was next boiled for more than 20 minutes and thus the sol was prepared in the hot condition. In the following tables the results are given when the sols prepared in the cold as well as in the hot are coagulated by bivalent anions, as both the sols could not be coagulated by even 2*N* KCl, 2*N* KBr etc.

TABLE IV.

Coagulation of chromium hydroxide prepared in the cold.

Concentration of the sol=1·725 gm. Cr_2O_3 per litre.
Amount taken each time=2 c.c.
Volume=5 c.c. Time=1 hour.

Electrolyte.	Concentration.	Amount to coagulate in c.c.	Precipitation value.
K_2F_2	N/15·12	1·00	0·0132
K_2SO_4	N/50	0·80	0·0032
$K_2C_2O_4$	N/50	0·95	0·0038
Sodium tartrate	N/50	0·80	0·0032

The precipitation values are in the following increasing order:—
sulphate > tartrate > oxalate > fluoride.

TABLE V.

Coagulation of boiled chromium hydroxide sol.

Concentration of the sol=1·725 gm. Cr_2O_3 per litre.
Amount of sol taken each time=2 c.c.
Volume=5 c.c. Time=1 hour.

Electrolyte.	Concentration.	Amount to coagulate in c.c.	Precipitation value.
K_2F_2	N/15·12	0·80	0·0105
K_2SO_4	N/50	0·70	0·0028
$K_2C_2O_4$	N/50	0·80	0·0032
Sodium tartrate	N/50	0·75	0·0030

The precipitation values are in the following increasing order:—
sulphate > tartrate > oxalate > fluoride.

(3) *Aluminium hydroxide sol.*

The sol was prepared by adding an excess of CH_3COONa to a solution of aluminium nitrate and then dialysing the mixture till it was free from electrolytes. The sol thus prepared in the cold was next boiled in order to obtain the sol in the hot condition. Like chromium hydroxide sols both the sols of aluminium hydroxide

could not be coagulated by concentrated solutions of KCl, KBr and KI. The following are the results obtained when the sols of $Al(OH)_3$ are coagulated by bivalent anions.

TABLE VI.

Coagulation of aluminium hydroxide sol prepared in the cold.

Concentration of the sol=1·32 gms. Al_2O_3 per litre.
Amount of sol taken each time=2 c.c.
Volume=5 c.c. Time=1 hour.

Electrolyte.	Concentration.	Amount to coagulate in c.c.	Precipitation value.
K_2F_2	N/37·8	1·65	0·0085
K_2SO_4	N/50	0·85	0·0035
$K_2C_2O_4$	N/50	1·00	0·0040
Sodium tartrate	N/50	0·90	0·0036

The precipitation values are in the following increasing order:—
sulphate > tartrate > oxalate > fluoride.

TABLE VII.

Coagulation of boiled sol of aluminium hydroxide.

Concentration of the sol=1·32 gm. Al_2O_3 per litre.
Amount of sol taken each time=2 c.c.
Volume=5 c.c. Time=1 hour.

Electrolyte.	Concentration.	Amount to coagulate in c.c.	Precipitation value.
K_2F_2	N/37·8	1·50	0·0079
K_2SO_4	N/50	0·75	0·0030
$K_2C_2O_4$	N/50	0·90	0·0036
Sodium tartrate	N/50	0·80	0·0032

The precipitation values are in the following increasing order:—
sulphate > tartrate > oxalate > fluoride.

The experimental results show that the amounts of electrolytes necessary for coagulatiug the sols prepared in the hot and cold conditions are very slightly different. In all cases the amounts of electrolytes necessary to coagulate a sol obtained in the hot condition is

slightly smaller than those required for the sols prepared in the cold. This is possibly due to the fact that the stabilising electrolytes adsorbed by the sols are smaller in the cases of those prepared in the hot than those obtained in the cold. Hence these results support the conclusion that the stability of a sol is not associated with its amount of hydration.

It will be interesting to note that zirconium hydroxide prepared in the hot and cold conditions form stable jellies. Similarly, we have shown that silicic acid sols prepared at the ordinary and the boiling temperatures also form jellies. Ceric hydroxide sol on the other hand forms jellies only from the sols prepared in the cold. From our measurements (*Z. anorg. Chem.*, 1927, **168**, 209) of viscosity of silicic acid we find that the viscosities of the two sols are not very different. The viscosity of the ceric hydroxide sol prepared in the hot is, however, much smaller than that of the sol obtained in the cold. We have now measured the viscosities of the two sols of zirconium hydroxide and find that it is 0·00968 for the sol prepared in the cold containing 7·54 gms. of ZrO_2 per litre and 0·01068 for the sol prepared in the hot containing 8·5 gms. of ZrO_2 per litre at 30°, whilst that of water at the same temperature is 0·00803. Hence the viscosities of the sols prepared in two different conditions are not different and thus we obtain jellies in both the cases very readily. Moreover the following results (*J. Phys. Chem.*, 1926, **30**, 1646; *Kolloid. Zeit.*, 1927, **42** 124) show that as compared to the hydroxides of aluminium, iron and chromium the viscosity of zirconium hydroxide is appreciably greater.

TABLE VIII.

Temperature 30°.

Sol.	Concentration gms. per litre.	Viscosity.
Water	—	0·00803
$Zr(OH)_4$	7·54 gm. ZrO_2	0·00968
$Fe(OH)_3$	9·14 gm. Fe_2O_3	0·00886
$Al(OH)_3$	15·6 gm. Al_2O_3	0·00880
$Cr(OH)_3$	8·13 gm. Cr_2O_3	0·01079 at 23·1°
Water	—	0·00987 ,,

This greater viscosity of $Zr(OH)_4$ sol is associated with its property of forming jellies readily.

Viscosities of $Ce(OH)_4$ and V_2O_5 sols are much greater than those of hydroxides of iron, aluminium and chromium. We have shown that $Ce(OH)_4$ prepared in the cold and V_2O_5 sols from jellies more readily than the above hydroxides. Moreover, in a foregoing paper we (*Kolloid. Zeit.*, 1927, **42**, 124) have shown that for the same concentration, $Fe(OH)_3$ sol is more viscous than As_2S_3 sol and it is well known that As_2S_3 sol cannot form a jelly. Hence the foregoing results conclusively prove that the tendency to form a jelly and high viscosity are always associated with a greater degree of solvation.

The foregoing results show that the coagulating power of fluoride iron towards the positively charged hydroxide sols is of the same order as that of the bivalent ions like sulphate, oxalate and tartrate. In the cases of $Al(OH)_3$ and $Cr(OH)_3$, the coagulating power of fluoride ion is slightly less than those of sulphate, oxalate and tartrate. This is possibly due to the fact that a part of K_2F_2 is removed by the formation of complex fluorides. It is well known that stable complex salts of the type M_3AlF_6, M_3CrF_6 etc., are formed by the action of M_2F_2 on hydroxides or salts of aluminium and chromium. It seems certain that the fluoride ion exists in the bivalent condition in aqueous solutions and therefore exerts a coagulating effect of the same order as the bivalent ions, sulphate, oxalate and tartrate.

Summary.

(1) Experimental results on the coagulation of zirconium hydroxide sols prepared in the cold and hot conditions by chloride, bromide and iodide ions show that the precipitation values of these ions are greater in the case of the sol prepared in the cold than in the hot. The precipitation values of ferrocyanide, sulphate, oxalate, tartrate and fluoride ions are slightly greater in the case of zirconium hydroxide prepared in the cold than in the hot.

(2) Zirconium hydroxide sol requires smaller quantities of electrolytes in the diluted condition than in the concentrated and shows additive relationship when coagulated by a mixture of electrolytes.

(3) The precipitation values of sulphate, tartrate, oxalate, and fluoride ions are slightly greater in the cases of sols of chromium and

aluminium hydroxides prepared in the cold than those prepared in the hot condition.

(4) It seems that the stabilising electrolytes adsorbed by the sols are smaller in the case of those prepared in the hot than those obtained in the cold.

(5) The stability of a sol appears not to be associated with its amount of hydration.

(6) Zirconium hydroxides, prepared in the hot and cold conditions, have practically the same viscosity and form stiff jelly in both the cases. Viscosities of zirconium hydroxide, vanadium pentoxide, and ceric hydroxide are greater than those of ferric, chromium, and aluminium hydroxides. Jellies are formed more readily with the first group of hydroxides than with the second.

(7) Tendency to form a jelly and high viscosity are associated with higher degree of solvation of the sol and are the most important criteria of lyophile colloids.

(8) Fluoride ions exist in the bivalent condition (F_2'') in aqueous solution and exerts a coagulating effect of the same order as the bivalent ions, sulphate, oxalate, and tartrate.

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Acclimatization and Ionic Antagonism with Sheep Serum and other Colloids.

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W. Spring [*Bull. Acad. Roy. Belg.*, [3], **38**, 483 (1900)] and H. Freundlich [*Zeit. physikal Chem.*, **44**, 143 (1903)] and H. B. Weiser [*J. Phys. Chem.*, **23**, 399 (1921)] stated that the amount of electrolyte necessary for coagulation of a sol is greater when the addition of the electrolyte to the sol is slow and spread out for several days than when it is rapid and the coagulation is finished quickly. We [*J. Phys. Chem.*, **29**, 659 (1925); **31**, 649 (1927); *Kolloid-Z.*, **37**, 141 (1926)] have made a systematic investigation of this phenomenon of acclimatisation and have observed this phenomenon with sols of arsenious sulphide, antimony sulphide, mastic, gum dammar, Prussian blue, gold, ferric hydroxide, and positively charged manganese dioxide, when coagulated by electrolytes which yield similarly charged ions capable of being adsorbed by the sols.

We have also observed that in the coagulation of arsenious sulphide and antimony sulphide by strychnine hydrochloride, quinine hydrochloride, crystal violet and methylene blue, and negatively charged manganese dioxide by silver nitrate and cupric sulphate, *smaller* quantities of electrolytes are necessary when the addition is slow and spread out for a long time than when the coagulation is rapidly finished. We have termed this phenomenon as negative acclimatisation. We have shown that cause of positive and negative acclimatisation lies on the ratio of adsorption of positive and negative ions by the sol. When a sol does not adsorb similarly charged ions and an ion carrying the opposite charge is highly adsorbed, we always get the phenomenon of negative acclimatisation.

We [*J. Phys. Chem.*, **30**, 830 (1926) *Kolloid-Z.*, **29**, 346 (1926)] have shown that that sols like arsenious sulphide, antimony sulphide, Prussian blue, cupric ferrocyanide, gum dammar, mastic and gamboge are appreciably hydrolysed and the stability of these sols depends upon the degree of hydrolysis. Hydrogen ions markedly retard this hydrolysis and make the sols unstable.

We have also shown that the phenomenon of ionic antagonism observable with certain sols is more pronounced when the sols are diluted and also depends on the ratio of adsorption of two ions.

In this paper, we have investigated the influence of dilution on the phenomenon of acclimatisation with sols of arsenious sulphide, mastic and gum dammar. We have also studied the coagulation of sheep serum by a mixture of electrolytes and by the slow addition of acids and salts.

TABLE I.

Acclimatization of a concentrated arsenious sulphide sol.

Concentration of the sol=3·29 gms. As_2S_3 per litre. Amount of sol taken each time=2 c.c. Volume=6 c.c.

Time of observation=1 hr. after adding the last quantity of the electrolyte.

Electrolyte.	Amount to coagulate when the electolyte is added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when added slowly.	% Difference.
NaCl N/2	1·2 c.c.	0·2 c.c.	1·30 c.c.	+8·3
CH_3COONa N/2	2·1	0·3	2·50	+19·0
HCl N/4	1·6	0·3	1·40	−12·5
HNO_3 N/4	1·6	0·3	1·40	−12·5
H_2SO_4 N/4	1·65	0·3	1·50	−9·1
CH_3COOH N	2·9	0·4	2·70	−6·9

TABLE II.

Acclimatization of a dilute arsenious sulphide sol.

Amount of sol taken each time=0·5 c.c. Time of observation=1 hr. after the last quantity of the electrolyte is added. Volume =6 c.c.

Electrolyte.	Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when the addition is slow.	% Difference.
NaCl N/2	1·35 c.c.	0·2 c.c.	1·45 c.c.	+7·4
CH_3COONa N/2	2·50	0·3	3·00	+20·0
HCl N/4	1·60	0·3	1·30	−18·7
HNO_3 N/4	1·60	0·3	1·35	−15·6
H_2SO_4 N/4	1·65	0·3	1·40	−15·2
CH_3COOH 4N	3·00	0·4	2·65	−11·6

TABLE III.

Acclimatization of a concentrated mastic sol.

Concentration of the sol=4·26 gms. mastic per litre. Amount of sol taken each time=2 c.c. Time of observation=1 hr. after the last addition of the electrolyte. Volume=6 c.c.

Electrolyte.	Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when the addition is slow.	% Difference.
NaCl N	0·65 c.c.	0·1 c.c.	0·70 c.c.	+8·3
CH_3COONa N	1·85	0·3	2·05	+10·8
HCl N/100	1·20	0·2	1·10	−8·3
HNO_3 N/100	1·20	0·2	1·10	−8·3
H_2SO_4 N/100	1·25	0·2	1·15	−8·0

TABLE IV.

Acclimatization of a dilute mastic sol.

Amount of sol taken each time=1 c.c. Time of observation =1 hr. after the last addition of the electrolyte. Volume=6 c.c.

Electrolyte.	Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when the addition is slow.	% Difference.
NaCl N	1·05 c.c.	0·1 c.c.	1·15 c.c.	+9·5
CH_3COONa N	2·90	0·3	3·30	+13·9
HCl N/100	1·20	0·2	1·05	−12·5
HNO_3 N/100	1·20	0·2	1·05	−12·5
H_2SO_4 N/100	1·25	0·2	1·05	−16

TABLE V.

Acclimatization of a concentrated gum dammar sol.

Concentration of the sol=4·28 gms. gum dammar per litre.

Amount of sol taken each time=2 c. c. Time of observation= 1 hr. after the last addition of the electrolyte. Volume=6 c.c.

Electrolyte.		Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when added slowly.	% Difference.
NaCl	N	0·8 c.c.	0·1 c.c.	0·9 c.c.	+12·5
CH_3COONa	N	1·8	0·3	2·05	+13·9
HCl	N/100	1·10	0·2	1·00	−9·0
HNO_3	N/100	1·10	0·2	1·00	−9·0
H_2SO_4	N/100	1·20	0·2	1·10	−8·3

TABLE VI.

Acclimatization of a dilute gum dammar sol.

1 c.c. of the sol is taken each time. Volume=6 c.c. Time of observation=1 hour after the last addition of the electrolyte.

Electrolyte.		Amount to coagulate when the addition is all at once.	Quantity added at a time for slow addition.	Amount to coagulate when added slowly.	% Difference.
NaCl	N	1·5 c.c.	0·2 c.c.	1·65 c.c.	+10·0
CH_3COONa	N	2·95	0·4	3·4	+15·3
HCl	N/100	1·10	0·2	0·9	−18·2
HNO_3	N/100	1·10	0·2	0·9	−18·2
H_2SO_4	N/100	1·20	0·2	1·05	−12·5

The foregoing tables show that the phenomenon of negative acclimatization is observed with sols of mastic, gamboge and arsenious sulphide when coagulated by acids and the phenomenon is more pronounced in the dilute sols.

In the following tables we shall record our results on the coagulation of sheep serum by different salts and acids. 6 C.c. of serum when heated in a water-bath for 90° minutes left a residue of 3·38 gms. The viscosity of the serum at 30°=0·01345, whilst that of water at 30°=0·00803. 2 C.c. of original serum taken.

Total volume=10 c.c.

Time of observation=1 hour.

TABLE VII.

Coagulation by Salts.

Salts.		Amount required to coagulate in c.c.	Coagulating concentration.
Sodium acetate 3·4M	...	7·80	2·6520
Sodium tartrate 1·32M	...	6·90	1·8216
Potassium oxalate 1·5M	...	6·45	1·8350
Potassium fluoride 8·0N	...	1·90	1·5200
Cerous nitrate N/200	...	5·35	0·00267
Aluminium nitrate N/200	...	5·20	0·00260
Thorium nitrate N/200	...	5·60	0·00280

Hence the coagulating powers of different salts are in the following decreasing order:—

$Al(NO_3)$ > $Ce(NO_3)_3$ > $Th(NO_3)_4$ > K_2F_2 > sodium tartrate > $K_2C_2O_4$ > sodium acetate.

TABLE VIII.

Coagulation by Acids.

Acids.		Amount required to coagulate in c.c.	Coagulating concentration.
Nitric	N/200 ...	6·8	0·0034
Hydrochloric	N/200 ...	7·0	0·0035
Sulphuric	N/200 ...	7·2	0·0036
Phosphoric	N/50 ...	4·7	0·0094
Formic	N/50 ...	1·85	0·0037
Acetic	N/50 ...	1·90	0·0038
Monochloracetic	N/50 ...	1·80	0·0036
Dichloracetic	N/50 ...	2·0	0·0040
Trichloracetic	N/50 ...	2·0	0·0040
Oxalic	N/100 ...	3·2	0·0032
Tartaric	N/100 ...	4·0	0·0040
Citric	N/100 ...	2·8	0·0028

Hence the coagulating powers of different acids are in the following decreasing order :—

Citric > oxalic > nitric > hydrochloric > sulphuric > monochloracetic > formic > acetic > dichloracetic > trichloracetic > tartaric > phosphoric.

The influence of dilution towards the coagulation of the serum has also been investigated and the following results were obtained :—

Serum A=2 c. c. of original serum.

Total volume=10 c. c.

Time of observation=1 hour.

TABLE IX.

Electrolytes.	A/2 Serum.	A Serum.	3A/2 Serum.
Sodium acetate 3·4M	9·0 c. c.	7·8 c.c.	6·6 c.c.
Sodium tartrate 1·32M	7·5	6·9	6·65
Potassium fluoride 8N	2·15	1·9	1·8
Potassium oxalate 1·5M	6·8	6·45	6·0

TABLE X.

	A/5 Serum.	A Serum.
Cerous nitrate N/200	1·65 c.c.	3·35 c.c.
Aluminium nitrate N/200	1·5	3·2
Thorium nitrate N/200	1·7	5·6

TABLE XI.

Acids.		A/5 Serum.	A Serum.
Nitric	N/200	2·3 c.c.	6·8 c.c.
Hydrochloric	N/200	2·4	7·0
Sulphuric	N/200	2·5	7·2
Phosphoric	N/50	2·0	4·7
Formic	N/50	0·50	1·35
Acetic	N/50	0·50	1·9
Monochloracetic	N/50	0·60	1·8
Dichloracetic	N/50	0·60	2·0
Trichloracetic	N/50	0·65	2·0
Oxalic	N/100	0·70	3·2
Tartaric	N/100	0·85	4·0
Citric	N/100	0·85	2·8

The above Tables IX, X and XI show that serum becomes more stable towards dilution when coagulated by salts of monovalent cations as sodium acetate, potassium fluoride, etc., whilst it behaves normally towards dilution when coagulated by either polyvalent cations or acids.

In the following tables the results are recorded when serum is coagulated by pairs of electrolytes.

2 C.c. of diluted (five times) serum taken.
Total volume ... 10 c.c.
Time of observation ... 1 hour.

TABLE XII.

Electrolytes added in c.c.		Amount of copper sulphate N/200 to coagulate in c.c.
—		0·20
0·2 c.c. of N/10 KOH	...	4·50
0·2 c.c. of 0·14M sodium citrate	...	1·90
0·1 c.c. of 1·78M sodium tartrate	...	4·00
0·20 c.c. of 3·46M sodium acetate	...	0·90

TABLE XIII.

Electrolytes added in c.c.		Amount of ferric chloride N/95·7 to coagulate in c.c.
—		0·20
0·2 c.c. of N/10 KOH	...	2·8
0·2 c.c. of 0·14M sodium citrate	...	6·3
0·2 c.c. of 0·178M sodium tartrate	...	2·5
0·2 c.c. of 3·46M sodium acetate	...	3·0

Thus, marked stabilisation has been observed when serum is coagulated by copper sulphate or ferric chloride in presence of very small quantities of potassium hydroxide, sodium acetate, tartrate, or citrate.

Coagulation by pairs of electrolytes.

2 C.c. of original serum taken.
Total volume ... 10 c.c.
Time of observation ... 1 hour.

TABLE XIV.

Sodium chloride + Cerous nitrate.

Amount of NaCl 0·1076N added in c.c.	Amount of cerous nitrate N/100 to coagulate in c.c.
0	4·10
8	0
0·2	4·40
0·50	4·70
1·0	4·85

TABLE XV.

Sodium chloride + Hydrochloric acid.

Amount of NaCl 0·1076N added in c.c.	Amount of HCl N/100 to coagulate in c.c.
0	3·6
8	0
0·2	3·95
0·5	4·30
1·0	5·25

TABLE XVI.

Barium chloride + Hydrochloric acid.

Amount of $BaCl_2$ 0·0855N added in c.c.	Amount of HCl N/100 to coagulate in c.c.
0	3·7
8	0
0·2	4·0
0·5	4·5
1·0	5·2

TABLE XVII.

Cerous nitrate + Hydrochloric acid.

Amount of HCl N/100 added in c.c.	N/100 cerous nitrate to coagulate in c.c.			% Difference.
	Observed.	Calculated.	Difference.	
0	3·05	—	—	—
3·7	0	—	—	—
0·2	2·9	2·85	+0·01	+0·03
0·5	2·75	2·65	0·1	+3·6
1·0	2·05	2·13	−0·08	−4

TABLE XVIII.

Potassium oxalate + Hydrochloric acid.

Amount of HCl N/100 added in c.c.	1·5M potassium oxalate to coagulate in c.c.			% Difference.
	Observed.	Calculated.	Difference.	
0	6·0	—	—	—
3·7	0	—	—	—
0·2	6·0	5·67	+0·33	+5·5
0·5	6·1	5·12	+0·88	+14·4
1·0	6·2	4·38	+1·82	+29·0

TABLE XIX.

Potassium fluoride + Hydrochloric acid.

Amount of HCl N/100 added in c.c.	8·0 *N* K_2F_2 to coagulate in c.c.			% Difference
	Observed.	Calculated.	Difference.	
0	1·9	—	—	—
3·7	0	—	—	—
0·2	1·95	1·8	+0·15	+7·7
0·5	1·90	1·75	+0·15	+7·9
1·0	1·9	1·59	+0·31	+16·0

TABLE XX.

Sodium chloride + Oxalic acid.

Amount of NaCl 0·1076*N* added in c.c.		Amount of oxalic acid N/100 to coagulate in c.c.
0	...	4·1
0·2	...	4·4
0·5	...	4·7
1·0	...	4·85

TABLE XXI.

Potassium fluoride + Dichloracetic acid.

Amount of dichloracetic acid N/50 added in c.c.	Amount of 8·0*N* K_2F_2 to coagulate in c.c.			%
	Observed.	Calculated.	Difference.	Difference.
0	1·9	—	—	—
2·0	0	—	—	—
0·2	1·9	1·71	+0·19	+10
0·5	1·9	1·42	+0·47	+25
1·0	1·9	0·95	+0·95	+50

TABLE XXII.

Trichloracetic acid + Sodium acetate.

Amount of trichloracetic acid N/50 added in c.c.	Amount of sodium acetate 4·07M to coagulate in c.c.			% Difference.
	Observed.	Calculated.	Difference.	
0	6·6	—	—	—
2·0	0	—	—	—
0·2	6·5	5·94	+0·56	+9·5
0·5	6·65	4·95	+1·70	+34·3
1·0	6·70	3·3	+3·4	+103·0

From Tables XIV to XXII, it is seen that antagonistic effect is observed when serum is coagulated with mixtures of sodium chloride + cerous nitrate, sodium chloride + HCl, $BaCl_2$ + HCl, $K_2C_2O_4$ + HCl, K_2F_2 + HCl, NaCl + $H_2C_2O_4$, K_2F_2 + dichloracetic acid, and trichloracetic acid + sodium acetate. When however, the serum is coagulated with mixtures of cerous nitrate and hydrochloric acid, additive amounts of these electrolytes precipitate the sol.

The phenomenon of acclimatisation has been studied with different acids and salts at different dilutions of the serum. In the following table, the results with acids and salts of polyvalent cations with a concentrated serum are recorded.

TABLE XXIII.

Original serum taken ... 2 c.c.
Total volume ... 10 c.c.
Time of acclimatisation experiments...6 hours.
Time of observation ... 1 hour after adding the last quantity of electrolyte.

Electrolytes.	Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when slowly added.	% Increment.
Nitric N/200 ...	6·8 c.c.	1 c.c.	8·5 c.c.	25
Hydrochloric N/200 ...	7·0	1	9·0	28·5
Sulphuric N/200 ...	7·2	1	9·4	30·5
Phosphoric N/50 ...	4·7	0·8	6·4	29·8
Formic N/50 ...	1·85	0·2	2·55	38·8
Acetic N/50 ...	1·9	0·25	3·0	57·8
Monochloracetic N/50 ...	1·8	0·3	2·70	50·0
Dichloracetic N/50 ...	2·0	0·3	2·45	22·0
Trichloracetic N/50 ...	2·0	0·3	2·4	20·0
Oxalic N/100 ...	3·2	0·4	4·9	53·1
Tartaric N/100 ...	4·0	0·5	6·3	57·5
Citric N/100 ...	2·8	0·2	3·7	32·1
Aluminium nitrate N/200	5·2	0·7	9·7	86·5
Cerous nitrate N/200 ...	5·35	0·7	8·9	66·3
Thorium nitrate N/200 ...	5·6	0·7	8·4	50·0

We shall now give our results with diluted serum where the phenomenon of acclimatization is studied with acids and salts of polyvalent cations.

TABLE XXIV.

2 C. c. of diluted (five times) serum taken.

Electrolytes.	Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when slowly added.	% Increment.
Nitric N/200	2·3 c. c.	0·3 c. c.	2·6 c. c.	13
Hydrochloric N/200	2·4	0·3	2·7	12·5
Phosphoric N/50	2·0	0·3	2·35	17·5
Formic N/50	0·5	0·05	0·65	30·0
Acetic N/50	0·5	0·05	0·65	30·0
Monochloracetic N/50	0·6	0·05	0·75	25·0
Dichloracetic N/50	0·6	0·05	0·70	16·6
Trichloracetic N/50	0·65	0·05	0·75	15·4
Oxalic N/100	0·75	0·1	1·05	40·0
Tartaric N/100	0·85	0·1	1·10	29·0
Citric N/100	0·85	0·1	0·95	11·8
Aluminium nitrate N/200	1·5	0·2	2·2	46·6
Cerous nitrate N/200	1·65	0·2	2·3	39·4
Thorium nitrate N/200	1·7	0·2	1·8	5·9

The results on acclimatization in presence of salts of univalent cations with concentrated and dilute serums are given below:

2 C.c. of original serum taken.

Serum A/2—when 1 c.c. of original serum used in experiments with dilute serum.

Time of observation—1 hour after adding the last quantity of electrolyte.

Time of acclimatization experiments—7 hours.

Total volume—10 c.c. when all electrolyte was added at once.

TABLE XXV.

With Serum A.

Electrolytes.	Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when slowly added.	% Increment.
Sodium acetate 4·07 M	6·6 c. c.	1·0 c. c.	17 c. c.	175
Sodium tartrate 1·32 M	6·9	1·0	11·3	63·7
Potassium flouride 8 N	1·9	0·2	1·9	0
Potassium oxalate 1·5 M	6·45	0·8	6·4	−0·8

TABLE XXVI.

With Serum A/2.

Electrolytes.	Amount to coagulate when added all at once.	Quantity added at a time for slow addition.	Amount to coagulate when slowly added.	% Increment.
Sodium acetate 4·07 M	7·4 c. c.	1·5 c. c.	19·5 c. c.	...
Sodium tartrate 1·32 M	7·5	1·0	13·2	76
Potassium flouride 8N	2·1	0·2	2·1	0
Potassium oxalate 1·5M	6·8	0·8	6·95	2·2

It will be seen that the percentage of positive acclimatization is more pronounced with a concentrated serum than a dilute one, when the coagulation is effected by acids and salts like aluminium nitrate, thorium nitrate, and cerous nitrate. On the other hand, this phenomenon is developed more with dilute serum than concentrated one with electrolytes like sodium acetate aud sodium tartrate. The phenomenon is, however, not at all developed with either potassium fluoride, or potassium oxalate. This seems to be due to the formation of insoluble calcium salts from the presence of calcium ions in sheep serum. The foregoing results are comparative as the serums used had the same p_H value.

We have shown in a previous paper that the relative checking of hydrolysis is greater when small amounts of an acid are used than when large amounts are added. Consequently, when small quantities of an acid are added to a hydrolysable sol, it will be rendered relatively more unstable and it coagulates more readily on further addition of an acid than when it is added all at once.

We have already shown that when arsenious and antimony sulphides, Prussian blue, cupric ferrocyanide, mastic, gamboge and gum dammar are coagulated by mixtures of an acid and a salt, the amount of salt necessary to complete the coagulation is much less than the additive amounts. It is clear, therefore, that with these sols the influence of the checking of hydrolysis in presence of acids is more important and more than counterbalances the effect of adsorption of similarly charged ions.

On the other hand, our experimental results show marked ionic antagonism when sheep serum is coagulated by mixtures of acid and salt and marked positive acclimatization is observed even when the serum is coagulated by acids. It is evident, therefore, that in the case of serum, the influence of similarly charged ions is more

important than the checking of the hydrolysis by acids. When, however, very diluted serums are used the hydrolysis of serum is increased and in these cases the amount of positive acclimatization is appreciably less than in the case of concentrated serum. The cases of negative acclimatization already observed by us in previous papers were due to the high adsorption of the oppositely charged ion in comparison with the adsorption of the similarly charged ion. The cases of negative acclimatization as observed in this paper are caused mainly by the redering of the sols unstable due to checking of hydrolysis by acids.

In a previous paper (*J. Phys. Chem.*, 1927, **31**, 187) we have shown that the sols of Prussian blue, mastic, gum dammar and gamboge require much larger quantities of a mono-valent salt in the diluted condition than the concentrated. The ionic antagonism, however, is not so highly developed with these sols. We are of the opinion that on dilution these hydrolysable sols become stable due to two causes: (1) The increase in the degree of hydrolysis and (2) the increase in the ratio of the adsorption of the negative to that of the positive ion. We have already quantitatively shown that the above sols are more hydrolysed than sols of either arsenious or antimony sulphides.

In the case of ionic antagonism when the sols are coagulated by mixtures of electrolytes, in the decrease of viscosity of sols on the addition of small amounts of electrolytes and in the phenomenon of positive acclimatization the influence of similarly charged ions is the dominant factor.

It has been shown in this laboratory that blood behaves as a sol capable of adsorbing similarly charged ions. Our experimental results on the coagulation of serum indicate that serum is also capable of adsorbing similarly charged ions and hence dilute serum is more stable towards electrolytes than concentrated serum. The phenomena of ionic antagonism and positive acclimatisation are also evident in this colloid. Serum, however, appears not to be hydrolysed to the same extent as the gums, Prussian blue, copper ferrocyanide and arsenious sulphide and possibly does not adsorb the coagulating ion very highly and consequently the phenomenon of negative acclimatisation is not observed in the coagulation of serum by different acids. In this case the capacity of adsorbing similarly charged ions is highly developed and in all cases we observe the phenomenon of positive acclimatisation and ionic antagonism.

Freundlich's ("Kappillar-Chemie", 1922, p. 628) explanation of positive acclimatisation based on the difference in the rates of diffusion of the added electrolytes when the addition is rapid and slow is untenable because the mixtures are always stirred and thoroughly mixed.

Weiser (*Z. physikal. Chem.*, 1926, **30**, 20) has tried to explain the phenomenon of acclimatisation from the view-point of the adsorption of electrolytes by the coagulated mass. From our experiments on the adsorption of electrolytes by precipitated substances, we find that ferric hydroxide is a better adsorbent than arsenious sulphide. Moreover, partial coagulation takes place with both the sols of ferric hydroxide and arsenious sulphide. Hence Weiser's view cannot explain the occurrence of the phenomenon more markedly with arsenious sulphide sol than with ferric hydroxide sol when coagulated by KCl, K_2SO_4 and $BaCl_2$.

According to Bancroft ("Applied Colloid Chemistry", 1921, p. 220) the first addition of an electrolyte causes a slight agglomeration, which is not sufficient to cause precipitation, but which cuts down the adsorbing power of the colloid, so that more salt is necessary to cause the same amount of adsorption. Now if the explanation of Bancroft be correct, the adsorption of barium ions by a sol of arsenious sulphide should be less when the addition is slow than when it is rapid, provided the same amount of the electrolyte is added in both the cases. We have, however, shown from adsorption experiments on the coagulation of arsenious sulphide that the adsorption of barium ions is much greater when the addition is slow than when it is rapid. Hence Bancroft's explanation is unsound.

We have already explained the phenomenon of positive acclimatisation from the point of view of the adsorption of similarly charged ions. When drops of barium chloride are added to a sol of arsenious sulphide, the sol is appreciably stabilised by the adsorption of chloride ions and hence greater quantities of barium chloride are necessary to coagulate the sol completely. From our experiments we have shown that the adsorption of barium ions is greater when the addition is slow than when it is rapid, simply because when small quantities of barium chloride are added to arsenious sulphide, the charge on the particle of the sol is increased by adsorption of chloride ions and hence greater amount of adsorption of barium ions is necessary to coagulate the sol.

We were the first to observe the phenomenon of negative acclimatisation and to offer an explanation of this interesting phenomenon, which is inexplicable from the views of Weiser and Bancroft. We have carried on quantitative experiments on the adsorption of silver and cupric ions in the slow and rapid coagulations of manganese dioxide sol by silver nitrate and cupric sulphate, and in these cases the phenomenon of negative acclimatisation has been observed.

25 C.c. of manganese dioxide containing 1 gm. MnO_2 per litre were rapidly mixed and coagulated with 14 c.c. N/100 $AgNO_3$ when 1·28 millimoles of Ag were adsorbed by the sol. On the other hand, 1·25 millimoles of Ag were adsorbed by the same amount of manganese dioxide when 13 c.c. of N/100 $AgNO_3$ were added slowly, 1. c.c. of the solution being added to the sol at a time. With $CuSO_4$ the adsorption of Cu ions was very high, the whole amount of the added copper salt was adsorbed by manganese dioxide sol at the precipitating concentration of $CuSO_4$ when the electrolyte is added either slowly or rapidly.

Our results with $AgNO_3$ prove that the percentage of adsorption of Ag is 91 when the addition of the electrolyte is rapid and it is 96 when the addition is slow, proving that when the addition is slow slightly smaller quantitites of the electrolyte would be sufficient to coagulate the sol and the phenomenon of negative acclimatization would develop. We have also observed that in the coagulation of arsenious sulphide and antimony sulphide by crystal violet, methylene blue, etc. the phenomenon of negative acclimatization is developed and these coagulating agents are completely adsorbed by the sol at the precipitating concentrations. These results are also interesting from the point of view that the phenomenon of negative acclimatization will be observed only in those cases where the adsorption of the oppositely charged ion is very prominent and the adsorption of the ion carrying the same charge is practically negligible.

Summary.

1. The phenomenon of acclimatization has been studied with concentrated and diluted sols of arsenious sulphide, mastic and gamboge. In all cases negative acclimatization has been observed when the sols are coagulated by acids. This is more marked with a dilute sol than a concentrated one.

2. Polyvalent cations and acids possess high coagulating powers towards sheep serum. The stability of a diluted serum towards its coagulation by univalent ions from salts like sodium acetate, potassium fluoride, potassium oxalate, etc., is far greater than a concentrated serum. On the other hand, smaller amounts of acids and polyvalent cations coagulate a dilute serum than a concentrated one.

3. Ionic antagonism is developed when serum is coagulated by mixtures of cations of varying valencies or an acid and a salt.

4. The phenomenon of positive acclimatization is observed when serum is coagulated by either acids or salts and it is more marked with salts than with acids. With potassium fluoride and potassium oxalate, no positive acclimatization is observed because of the formation of calcium fluoride and oxalate from the calcium ions present in serum. The phenomenon of acclimatization is more marked for the dilute serum than the concentrated one when coagulated by salts. With acids the phenomenon is less developed with dilute serum.

5. Sheep serum, therefore, behaves in certain respects, like sols of mastic, gamboge, arsenious sulphide, etc. and is capable of adsorbing similarly charged ions from coagulating electrolytes. It is however not hydrolysed to the same extent as the gums, Prussian blue, and cupric ferrocyanide and possibly does not adsorb the coagulating ion very highly.

6. The phenomenon of negative acclimatization observed in the coagulation of the highly hydrolysable sols (gum dammar, gamboge, mastic, etc.) by acids originates from the checking of hydrolysis of the sols by acids.

7. Ionic antagonism, decrease of viscosity of sols in presence of small amounts of electrolytes and positive acclimatization are due mainly to the adsorption of similarly charged ions. The abnormal dilution effect of hydrolysable sols is due to two causes: (1) Increase in the degree of hydrolysis of the sols on dilution and (2) the increase in the ratio of the adsorption of the negative to that of the positive ion on dilution.

8. The phenomenon of negative acclimatization first observed in this laboratory cannot be explained from the view-points of Freundlich, Bancroft and Weiser and depends on the high adsorbability of the coagulating ion by the sol. This phenomenon will only be observed in those cases where the adsorption of the oppositely charged ions is very high and that of the similarly charged ions is negligible.

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On the Applicability of Fresnel's Law in Deducing Evidence in Favour of Surface Structure from Surface Reflectivity.

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Fresnel, from considerations of the electro-magnetic theory of light, worked out an equation for calculating the energy in the reflected ray, when the incident light is unpolarised.

The equation is:

$$I=\tfrac{1}{2}a^2\left[\frac{\sin^2(i-r)}{\sin^2(i+r)}+\frac{\tan^2(i-r)}{\tan^2(i+r)}\right]$$

where I = the intensity of the reflected ray;
a = amplitude of incident vibration;
i and r = the angles of incidence and refraction respectively.

This equation, however, postulates a sudden change in physical properties in passing from one medium to another and a similar uniform arrangement of molecules throughout the bulk as also on the surface of the liquid. But from the work of Langmuir, *J. Amer. Chem. Soc.*, 1917, **39**, 1848; *Chem. and Met. Eng.*, 1916, **15**, 468; Harkins, *J. Amer. Chem. Soc.*, 1917, **39**, 541; Adams, *Proc. Roy. Soc.*, 1921, **99A**, 336; 1922, **101A**, 452, 516) and others on the orientation of surface molecules in a liquid, it is clear that the arrangement of molecules at the surface is quite different from what it is in the bulk. The polar groups like OH, COOH, NH_2, etc., are supposed to be pointing downwards towards the bulk of the liquid, leaving the non-polar groups floating on the surface. If this be so it would be interesting to find out if some deviations from the Fresnel's equation would be observed in the case of reflection from liquid surfaces which are known to have a definite surface orientation. It was with this view that the present investigation was undertaken to explore the limits of applicability of the Fresnel's equation in the case of liquids, on the assumption that the first reflection from the liquid surface takes place from the molecules in the surface layer.

Experimental.

The intensity of the reflected ray of light was measured by the Boys' radiomicrometer manufactured by Cambridge Instrument Co. The arrangements made for the experiments are shown in Plate I. They consisted of devices—

(1) to take the incident beam of light ;

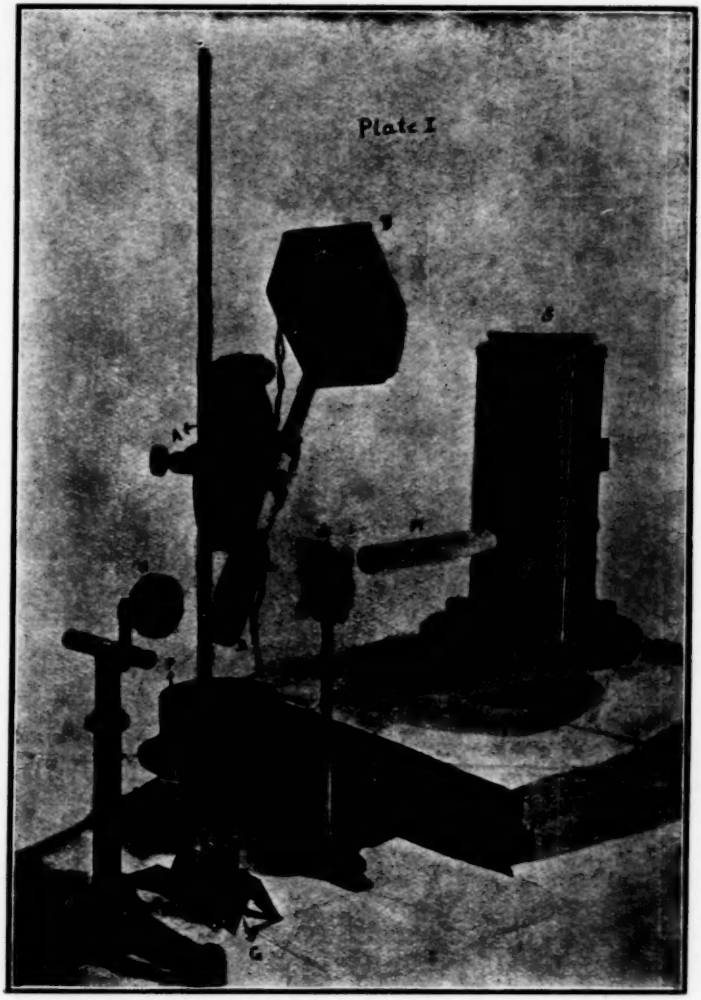
(2) to put the liquid, whose surface-reflectivity was to be examined in a suitable manner in a non-reflecting vessel ;

(3) to focus the reflected ray on the receiving plate of the Boys' radiomicrometer.

(1) *To take the incident beam of light.*

The arrangement for the incident beam of light was such that the light could be arranged to fall on the liquid surface at any desired angle to the normal. For this purpose a theodolite scale was used. It was graduated into 360 divisions, each division representing a degree. A tangent screw with a graduated head was also attached to the scale which had to be released for moving the scale independent of it. One full turn of the screw head rotated the scale through one degree and graduations on it were such that readings could be taken with an accuracy of about 1′. At the centre of the scale was carefully fixed a metallic tube of 1·5 cm. diameter in such a way that when it was vertical as seen by the spirit levels fixed on the surface of the scale, the reading on it as well as on the graduated head of the tangent screw was zero. After this the tangent screw was moved until the tube became horizontal as shown by the spirit levels, when the angle reading was found to be 90°. This confirmed the initial setting of the tube. Later on adjustments of angles were made by the tangent screw only.

On one end of the tube was soldered a metallic disc which had a circular hole of 3 mm. diameter bored into it. This end of the tube carried a small wooden box, in which was fixed a small 12 volt, 21 c.p. bulb in such a way that the light from a small portion of the filament only could pass through the small hole in the disc, attached to the tube. The other end of the tube carried a brass head soldered to it. Into this head was fitted another metallic tube which could smoothly slide into it. The outer end of the sliding tube was closed by means of a metallic disc which had a circular hole of 4 mm. diameter accurately bored into its centre. This tube carried a lens



A = Theodolite scale for measuring the angles of incidence.
B = A wooden box containing a 12 volt 21 c. p. half-watt bulb.
C = A brass head.
D = A brass tube sliding into C.
E = Watch glass on which the liquid is placed.
F = Wooden block on which a groove is cut to fit the watch glass.
G = Adjustable table.
H = Plane mirror capable of moving both on its horizontal and vertical axes.
L = Lens to focus the reflected ray to the thermopile.
M = Tube containing several diaphragms.
S = Boys' radiomicrometer.

in it to give a parallel beam of incident light. The sliding tube was pushed in or out until the distance between the source of light and the lens was equal to the focal length (36 cm.) of the latter. The parallelism of the emergent beam was tested by means of a telescope focussed for infinity.

All the tubes and the box containing the bulb were coated on the inner surfaces with a dull black paint to avoid all reflections from surfaces. The scale with all the arrangements described above carried a clamping device so that the whole thing could be raised or lowered or rotated as desired. The stand carrying it was rigidly fixed on a wooden base board which was placed on a stone table, so that the liquid surface was not disturbed by any external vibration.

(2) *The arrangement for placing the liquid whose surface reflectivity was to be examined in a suitable vessel.*

The liquid was put on a shallow watch glass which was finely ground both on its inner and outer surfaces. The outer surface was coated with a dull black paint to reduce the reflection from the liquid glass interface to a minimum, and thus only the first reflection from the liquid surface was examined. In order that the watch glass may be put in the same position in all the experiments, a groove was carefully cut in a block of wood in which the watch glass fitted exactly. The latter rested on a metallic support that could be adjusted at any height. This was also rigidly fixed to the base board.

(3) *To focus the reflected ray on the receiving plate of the Boys' radiomicrometer.*

The ray of light after being reflected from the liquid surface was made to fall on a plane mirror of small aperture, which was capable of movement both on the horizontal and vertical axes. The mirror was clamped in a stand which could be adjusted laterally as also vertically and was thus rendered capable of all sorts of motions, helping thereby in adjustment to throw the reflected ray horizontally on to the receiving plate of the radiomicrometer. After the second reflection from the mirror the ray was focussed on the receiving plate by means of a lens whose focal length was equal to the distance between the lens and the receiving plate.

To get rid of other external radiations a tube carrying four or five diaphragms of gradually decreasing diameters was fitted into the

radiomicrometer. The range of these diameters varied from 3 cms. at the outer end to 5 mms. at the inner one, which in this way allowed only a horizontal ray to pass through it and fall on the thermopile. Proper adjustments of the reflecting mirror were made to give a perfectly horizontal beam, which after passing through all these diaphragms could be seen as a bright circular patch of light with the shadow of the receiving plate at the centre, on a ground glass plate placed at the opening provided in the instrument for observations, opposite to the one carrying the tube. The next step was to focus the circular patch on the plate by the lens and the patch thus obtained was just big enough to cover the receiving plate. No portion of the light was allowed to fall outside of it. The deflections obtained were noted on a scale put at a distance of a metre from the radiomicrometer. These deflections were taken to be proportional to the intensity of the reflected ray of light.

The liquids used in the investigation were either Kahlbaum's or Merck's extra pure chemicals. Some of them had to be specially purified for this work by repeated distillations or crystallisation. They were all freshly distilled just before use and the refractive index of the liquid for the light used in our experiment was determined by the Abbe refractometer. This was necessary to determine the Brewsterian angle for the liquid and served as an evidence of the purity of the substance. The experiments were carried on in a constant temperature room.

Before examining the reflected ray from a liquid surface at any particular angle, the reflected ray at that angle from the water surface was first examined. This reading was taken as the standard in terms of which the deflections of the new liquid was expressed. Thus if at an angle θ, I_1 and I_2 be the intensities of the reflected rays in the case of a liquid and water respectively, and d_1 and d_2 be the corresponding deflections, then

$$I_1 = K.\, d_1$$
$$\text{and } I_2 = K.\, d_2,$$

$$\therefore \frac{I_1}{I_2} = \frac{d_1}{d_2}.$$

(where K the constant will remain the same in both the cases).

To note the deflection due to the reflected ray from the water surface, it was freshly distilled every time before use. Some of it was poured on the clean dry watch glass and the surface was made

to overflow after which the liquid was thrown away. This was done to ensure the absence of any dust particles sticking on the watch glass and also to guard against lens formation. The watch glass was next put into the groove on the block of wood and 2 c.c. of water were accurately measured into it. All the necessary adjustments described above were made as soon as possible and deflections were observed. No readings were considered unless they could be repeated at least five times.

To get the deflection from a liquid surface the watch glass was removed from the groove and dried by blowing a current of hot air over it. It was then cooled, rinsed with a few drops of freshly distilled liquid to be examined, and replaced in the groove, when 2 c. c. of the liquid were measured out in it and the deflections noted. The different angles at which the liquids were examined were 30°, 45°, 60°, 70° and also their respective Brewsterian angles. Angles below 30° could not be examined owing to the feeble intensity of the reflected ray and above 70°, the deflections were found to be very large. The results are enumerated in the following tables. Table I gives a few readings at random to show the range of variations in the deflections observed in any particular case.

TABLE I.

Liquid.	Angle of incidence.	Deflections observed (in cms).					
		(1)	(2)	(3)	(4)	(5)	Mean.
Water ...	70°	29·75	29·75	29·70	29·75	29·70	29·73
Methyl acetate ...	65°	20·35	20·35	20·35	20·35	20·35	20·35
Ethyl alcohol ...	60°	12·85	12·85	12·85	12·85	12·85	12·85
Toluene ...	45°	9·00	9·00	9·00	9·00	9·00	9·00
Dimethyl aniline ...	30°	8·60	8·60	8·60	8·60	8·60	8·60

In Table II are given the deflections observed in the case of various liquid surfaces at their respective Brewsterian angles.

TABLE II.

Liquids.	Brewsterian angle.	Deflection in cms.	Ratio of the deflection observed in the case of liquid to the corresponding water deflection.
Water ...	53°5′	7·75	1·000
Ethyl alcohol ...	53°42′	9·20	1·125
n-Propyl alcohol	54°6′	9·46	1·245
iso-Propyl ,,	53°57′	9·00	1·200
n-Butyl ,,	54°22′	9·90	1·269
iso-Butyl ,,	54°17′	9·82	1·271
n-Amyl ,,	54°32′	10·15	1·269
Dimethyl ethyl carbinol ...	54°30′	10·45	1·259
Acetic acid ...	53°55′	9·28	1·167
Propionic acid ...	54°10′	9·90	1·222
n-Butyric acid ...	54°38′	10·55	1·302
iso-Butyric acid	54°19′	10·20	1·241
Benzene ...	56°16′	13·95	1·550
Toluene ...	56°9	14·40	1·532
m-Xylene ...	56°4′	14·25	1·524
Methyl acetate ...	53°38′	8·85	1·141
Ethyl acetate ...	53°50′	9·17	1·183
Propyl acetate ...	54°5′	9·90	1·214
iso-Butyl acetate	54°12′	10·13	1·213
Ethylene chloride	55°13′	12·60	1·403
Aniline ...	57°40′	18·05	1·750
Ethyl aniline ...	57°10′	17·20	1·686
Dimethyl aniline	57°13′	16·70	1·704
Diethyl aniline ...	56°57′	16·5	1·659
Toluidine ...	57°27′	17·2	1·720
Dimethyl toluidine. ...	56°41′	15·55	1·637
Copper ferrocyanide sol.	53°5′	7·75	1·000
Gelatine sol	53°5′	7·75	1·000

Tables III-VII give the value of the ratio between the deflection noted in the case of the liquid to that in the case of the water at the same angle for different groups of substances. Side by side with the experimental values are given the values of the ratio as calculated from the Fresnel's formula.

If I_1 be the intensity of the reflected ray from a liquid surface at an angle of incidence i and I_2 be that in the case of water at the same angle and if r_1, r_2 be the respective angles of refraction, we have

$$I_1=\frac{1}{2}a^2\left[\frac{\sin^2(i-r_1)}{\sin^2(i+r_1)}+\frac{\tan^2(i-r_1)}{\tan^2(i+r_1)}\right]$$

$$\text{and } I_2=\frac{1}{2}a^2\left[\frac{\sin^2(i-r_2)}{\sin^2(i+r_2)}+\frac{\tan^2(i-r_2)}{\tan^2(i+r_2)}\right].$$

(a will be the same in both the cases because the source of light is the same).

$$\therefore \frac{I_1}{I_2}=\frac{\dfrac{\sin^2(i-r_1)}{\sin^2(i+r_1)}+\dfrac{\tan^2(i-r_1)}{\tan^2(i+r_1)}}{\dfrac{\sin^2(i-r_2)}{\sin^2(i+r_2)}+\dfrac{\tan^2(i-r_2)}{\tan^2(i+r_2)}}$$

Now, intensity of the light can be taken proportional to the deflections observed.

$$\therefore \frac{I_1}{I_2}=\frac{d_1}{d_2}=\frac{\dfrac{\sin^2(i-r_1)}{\sin^2(i+r_1)}+\dfrac{\tan^2(i-r_1)}{\tan^2(i+r_1)}}{\dfrac{\sin^2(i-r_2)}{\sin^2(i+r_2)}+\dfrac{\tan^2(i-r_2)}{\tan^2(i+r_2)}}$$

From this it is clear that if Fresnel's formula holds in the case of liquids examined, we should have the ratio of the deflections observed in the case of a liquid to that in the case of water under similar conditions, equal to the ratio of the intensities in the two cases as calculated from the formula.

In the following tables are given the results obtained with alcohols, saturated carboxylic acids, esters, aromatic hydrocarbons and aromatic amines.

Table III.

Alcohols.

Alcohols.	Angle 70° Obs. $\frac{d_1}{d_2}$	Angle 70° Calc. $\frac{I_1}{I_2}$	Angle 70° Percentage difference.	Angle 65° Obs. $\frac{d_1}{d_2}$	Angle 65° Calc. $\frac{I_1}{I_2}$	Angle 65° Percentage difference.	Angle 60° Obs. $\frac{d_1}{d_2}$	Angle 60° Calc. $\frac{I_1}{I_2}$	Angle 60° Percentage difference.
Ethyl alcohol ...	1·088	1·056	+3·03	1·096	1·072	+2·24	1·105	1·091	+1·28
Propyl alcohol ...	1·105	1·095	+0·91	1·185	1·121	+5·71	1·191	1·153	+3·295
iso-Propyl alcohol	1·104	1·081	+2·13	1·120	1·106	+1·27	1·157	1·132	+2·21
Butyl alcohol ..	1·138	1·119	+1·698	1·165	1·155	+0·87	1·214	1·168	+3·94
iso-Butyl alcohol	1·112	1·112	0·000	1·162	1·147	+2·18	1·213	1·182	+2·62
Amyl alcohol ...	1·148	1·134	+1·23	1·193	1·176	+1·45	1·236	1·221	+1·23
Dimethyl ethyl carbinol ...	1·120	1·132	−1·06	1·174	1·172	+0·17	1·221	1·216	+0·37

Table III (*Continued*).

Alcohols.

Alcohols.	Angle 45° Obs. $\frac{d_1}{d_2}$	Angle 45° Calc. $\frac{I_1}{I_2}$	Angle 45° Percentage difference.	Angle 30° Obs. $\frac{d_1}{d_2}$	Angle 30° Calc. $\frac{I_1}{I_2}$	Angle 30° Percentage difference.
Ethyl alcohol ...	1·162	1·131	+2·74	1·184	1·152	+2·78
Propyl alcohol. ...	1·296	1·227	+5·62	1·318	1·256	+5·095
iso-Propyl alcohol ...	1·261	1·196	+5·43	1·294	1·217	+6·33
Butyl alcohol ...	1·382	1·296	+6·63	1·429	1·336	+6·96
iso-Butyl alcohol ...	1·378	1·244	+2·73	1·145	1·313	+10·43
Amyl alcohol ...	1·387	1·336	+3·82	1·460	1·382	+5·64
Dimethyl ethyl carbinol ...	1·350	1·325	+1·89	1·408	1·371	+2·699

Table IV.

Acids.

Acids.	Angle 70° Obs. $\frac{d_1}{d_2}$	Angle 70° Calc. $\frac{I_1}{I_2}$	Angle 70° Percentage difference.	Angle 65° Obs. $\frac{d_1}{d_2}$	Angle 65° Calc. $\frac{I_1}{I_2}$	Angle 65° Percentage difference.	Angle 60° Obs. $\frac{d_1}{d_2}$	Angle 60° Calc. $\frac{I_1}{I_2}$	Angle 60° Percentage difference.
Acetic acid ...	1·076	1·077	−0·093	1·104	1·099	+0·46	1·152	1·124	+2·49
Propionic acid	1·109	1·102	+0·64	1·144	1·132	+1·06	1·170	1·165	+0·43
n-Butyric acid	1·160	1·142	+1·58	1·189	1·188	+0·08	1·250	1·236	+1·13
iso-Butyric acid	1·119	1·114	+0·45	1·153	1·148	+0·44	1·189	1·185	+0·34

TABLE IV (*Continued*).

Acids.

Acids.	Angle 45° Obs. $\frac{d_1}{d_2}$	Angle 45° Calc. $\frac{I_1}{I_2}$	Angle 45° Percentage difference.	Angle 30° Obs. $\frac{d_1}{d_2}$	Angle 30° Calc. $\frac{I_1}{I_2}$	Angle 30° Percentage difference.
Acetic acid ...	1·177	1·183	−0·42	1·216	1·205	+0·91
Propionic acid ...	1·295	1·247	+3·85	1·320	1·278	+3·26
n-Butyric acid ...	1·411	1·359	+3·83	1·732	1·414	+22·49
iso-Butyric acid ...	1·312	1·279	+2·58	1·320	1·319	+0·08

TABLE V.

Esters.

Name.	Angle 70° Obs. $\frac{d_1}{d_2}$	Angle 70° Calc. $\frac{I_1}{I_2}$	Angle 70° Percentage difference.	Angle 65° Obs. $\frac{d_1}{d_2}$	Angle 65° Calc. $\frac{I_1}{I_2}$	Angle 65° Percentage difference.	Angle 60° Obs. $\frac{d_1}{d_2}$	Angle 60° Calc. $\frac{I_1}{I_2}$	Angle 60° Percentage difference.
Methyl acetate	1·071	1·052	+1·81	1·082	1·067	+1·41	1·113	1·082	+2·87
Ethyl acetate	1·079	1·070	+0·84	1·114	1·091	+2·11	1·131	1·112	+1·71
Propyl acetate	1·101	1·095	+0·55	1·143	1·121	+1·96	1·166	1·153	+1·13
iso-Butyl acetate	1·107	1·106	+0·09	1·152	1·137	+1·32	1·186	1·172	+1·19

TABLE V (*Continued*).

Esters.

Esters.	Angle 45° Obs. $\frac{d_1}{d_2}$	Angle 45° Calc. $\frac{I_1}{I_2}$	Angle 45° Percentage difference.	Angle 30° Obs. $\frac{d_1}{d_2}$	Angle 30° Calc. $\frac{I_1}{I_2}$	Angle 30° Percentage difference.
Methyl acetate ...	1·155	1·119	+3·22	1·216	1·136	+7·04
Ethyl acetate ...	1·215	1·164	+4·38	1·238	1·184	+4·14
Propyl acetate ...	1·258	1·227	+2·53	1·289	1·256	+2·63
iso-Butyl acetate...	1·295	1·256	+3·11	1·329	1·290	+3·02

TABLE VI.

Aromatic Hydrocarbons.

Aromatic Hydrocarbon.	Angle 70°			Angle 65°			Angle 60°		
	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.
Benzene ...	1·251	1·281	−2·34	1·345	1·385	−2·89	1·453	1·494	−2·74
Toluene ...	1·248	1·272	−1·89	1·341	1·369	−2·05	1·442	1·476	−2·30
Xylene ...	1·227	1·265	−3·00	1·316	1·358	−3·09	1·429	1·463	−2·32

TABLE VI (*continued*).

Aromatic Hydrocarbons.

Aromatic Hydrocarbon.	Angle 45°			Angle 30°		
	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.
Benzene ...	1·780	1·800	−1·11	1·933	1·933	−0·05
Toluene ...	1·740	1·763	−1·30	1·890	1·889	+0·05
Xylene ...	1·726	1·739	−0·75	1·890	1·861	+1·56

TABLE VII.

Aromatic Amines.

Aromatic amines.	Angle 70°			Angle 65°			Angle 60°		
	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.
Aniline ...	1·321	1·388	−4·83	1·478	1·541	−4·09	1·647	1·714	−3·91
Ethyl aniline ...	1·310	1·351	−3·03	1·445	1·479	−2·30	1·580	1·636	−3·42
Dimethyl aniline	1·313	1·354	−3·03	1·442	1·490	−3·22	1·603	1·644	−2·49
Diethyl aniline ...	1·292	1·329	−2·78	1·418	1·461	−2·94	1·566	1·601	−2·19
Toluidine ...	1·326	1·373	−3·42	1·478	1·518	−2·64	1·640	1·682	−2·50
Dimethyl toluidine	1·278	1·313	−2·67	1·406	1·429	−1·61	1·536	1·557	−1·35

TABLE VII (*continued*).

Aromatic Amines.

Aromatic amines.	Angle 45°			Angle 30°		
	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.
Aniline ...	2·180	2·215	−1·58	2·453	2·439	+0·57
Ethyl Aniline ...	2·066	2·062	+0·19	2·273	2·256	+0·95
Dimethyl aniline	2·068	2·073	+0·72	2·294	2·274	+0·88
Diethyl aniline ...	2·018	1·995	+1·15	2·195	2·175	+0·92
Toluidine ...	2·153	2·153	+0·00	2·400	2·369	+1·31
Dimethyl toluidine	1·942	1·913	+1·52	2·174	2·072	+4·92

Summary and Discussion of Results.

From the tables it is clear that the calculated ratio of intensities I_1/I_2 is not equal to d_1/d_2 in all cases. This can be due to two possible causes:

1. To an error in the value of the angle observed.
2. To a variation in the refractive index of the liquid due to temperature or other causes.

The observed difference cannot be ascribed to the cause (1), as it can be seen that an error of at least more than 2° should be assumed to have occured to account for this difference. Such a large error in measuring the angle is not likely in the apparatus. The error of setting does not exceed 10′ and it is readily seen that this small difference will not appreciably change the calculated ratio. This will be clear from the following calculations for propyl alcohol:—

Angles.	Ratio (I_1/I_2).
60°6′	1·153
60°	1·153
59°52′	1·152

Any error in the re fractive index can only take place in either of the following ways:

1. The temperature not being constant in the course of the experiment.
2. The values of the refractive indices used may not be for the effective wave-lengths.
3. Presence of impurities in the substance.

As we have mentioned above the experiments were all carried out in a double walled underground room whose temperature variation was negligible during the interval of the experiments and further the refract ive indices of the liquids were determined immediately before use at room temperature by the Abbe refractometer, whose temperature was kept constant by means of a water circulating arrangement ; hence we think that no error due to this factor was possible.

As the liquids used in this investigation were extra pure chemicals of Kahlbaum or Merck, and in several cases special cares were taken to purify them, no error due to (3) is also present.

The source of light used was the same throughout and the battery maintained a constant voltage all along. Prof. Raman, in a private letter, has kindly drawn our attention to the advisability of taking for the refractive index the value for the infra-red region, as the radiomicrometer has a maximum sensitivity for those rays. We give below the calculated values for ethyl and propyl alcohols and also for benzene using the refractive index for $\lambda=1{\cdot}028$ and $0{\cdot}997\ \mu$.

TABLE VIII.

Name.	$\mu^{t^\circ}_{\lambda}$	Angle 70°			Angle 65°			Angle 60°		
		Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.
Ethyl alcohol	$\mu^{25^\circ}_{1{\cdot}028\mu}=1{\cdot}3521$	1·088	1·057	+2·93	1·096	1·074	+2·05	1·105	1·092	+1·19
Propyl alcohol	$\mu^{19^\circ{\cdot}5}_{1{\cdot}028\mu}=1{\cdot}3782$	1·105	1·106	−0·09	1·185	1·139	+4·04	1·191	1·172	+1·62
Benzene	$\mu^{25^\circ}_{\cdot 997\,\mu}=1{\cdot}4823$	1·251	1·279	−2·19	1·345	1·378	−2·40	1·453	1·488	−2·35

TABLE VIII (*continued*).

Name	Angle 45°			Angle 30°		
	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.
Ethyl alcohol ...	1·162	1·132	+2·65	1·184	1·182	+0·17
Propyl alcohol ...	1·296	1·256	+3·18	1·318	1·326	−0·60
Benzene ...	1·780	1·783	−0·17	1·932	1·967	−1·78

Fresnel's Law seems to hold for reflections from liquid surfaces within limits of reasonable accuracy. There are, however, several points of interest.

It is evident from Table VIII that the substitution of the values of refractive indices for larger wave-lengths changes the values of I_1/I_2 calculated on the Fresnel's Law in a manner that the agreement between these values and those experimentally deduced becomes much closer. The differences in some cases, however, are larger than can be ascribed to experimental error even after the correct value of μ in the infra-red region is taken into account and although the authors are not definite, they consider it possible that these differences may have a physical meaning. Their reasons for suspecting this are the following:

I. It is seen that the compounds having polar groups behave differently from those having no polar groups in the following respects:—

(*a*) In aliphatic compounds with polar groups the differences between the calculated and the observed values are always positive, *i.e.*, the observed value is greater than the calculated value.

(*b*) In compounds with no polar groups in them the calculated values are always greater than the observed values.

II. It is seen that the differences observed in the case of aliphatic compounds and aromatic amines, (*i.e.*, those substances which have got polar groups in them) are always greater than those of aromatic hydrocarbons, which contain no polar group.

III. In the two aromatic series examined, namely, the aromatic hydrocarbons and the amines, the values of I_1/I_2 observed are always

less than the calculated ones at higher angles of incidence. At smaller angels of incidence, the aromatic amines exhibit a positive difference which may be due to the presence of at least one orientating radical in them. In the aliphatic compounds the observed values are always greater than the calculated values.

IV. When comparing the mean deviation from the calculated values in the case of aromatic hydrocarbons and aromatic amines, the latter (which have a chance of assuming orientation) show always the greater deviation. If these small differences were due to error in experimentation they should have very little chance of exhibiting the regularities shown above.

Further work on the subject is in progress and an apparatus is being devised for using a bright monochromatic light in these investigations.

Investigations on the reflectivity of light from the surface of a colloidal solution are already under way and we hope to throw further light in the near future on the subject by trying various monochromatic lights from the ultra-violet to the infra-red region.

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On Photochemical Reaction between Bromine and Tartaric acid in Aqueous Solution. Part II.

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The photochemical reaction between bromine aud tartaric acid in aqueous solutions has previously been investigated in this laboratory (This *Journal*, 1925, **2**, 165). In view of some very interesting and peculiar results obtained therein we have thoroughly revised and enlarged the previous work. This and the next paper of the series will embody the results of our fresh investigations.

Experimental.

The experimental arrangement was exactly the same as before, only the Wratten filter was replaced by solutions of different substances in order to isolate different regions of wavelength. Our investigations show that the Wratten filter, previously used, transmitted a large amount of photochemically inactive rays so that the intensity of the photo-chemically effective rays was very small. This accounts for the very large periods of induction and small velocity constants obtained in the previous work.

Since withdrawal of 2 c.c. of the reaction mixture each time leaves a vacant space in the reaction cell ($4 \times 4 \times 1$ cm.) into which the bromine would evaporate, experiments were first made to find out if this would affect our readings. Experiments with a N/30 solution of bromine at 33° showed that the effect was negligible.

Experiments on the rate of hydrolysis of a N/30 bromine solution at 33° showed that the rate was negligible, the unimolecular constant falling off from 0·00028 to 0·000136 in four hours. Light did not accelerate the rate of hydrolysis.

2 C.c. of the reaction mixture were withdrawn at different intervals throughout the present investigation and titrated with N/200 thiosulphate.

The constants of the reaction, throughout this paper, are calculated on the basis of a unimolecular reaction with respect to bromine ($K=\frac{1}{t}\log_{10}\frac{a}{a-x}$), the time being reckoned in minutes.

The Dark Reaction.

The velocity of the dark reaction between bromine and tartaric acid solutions was found to be negligible in comparison with the light reaction and is characterised by very large induction periods. Table I gives the dark reaction.

TABLE I.

Tartaric acid—M/7·5. Bromine—N/30. Temp.—33·3°.

Time in mins.	N/200 Br.	Unimolecular constant.	Period of induction.
0	12·45 c.c.	—	
341	10·45	—	5½ hours.
375	10·1	·00044	
427	9·7	·00038	
500	9·05	·00039	

By raising the temperature to 48° the velocity constant increased to 0·0044 thus giving the very high value 4·6 as the temperature coefficient of the dark reaction.

The reaction was then carried out under the stimulus of light from a 1000 c.p. point-o-little lamp, rendered parallel by means of a lens. For the initial measurements only *N* KNO_3 (1 cm.) and *N*/20$CuSO_4$ (1 cm.) filters were employed to cut off the ultraviolet and the heat rays. Tables II-V indicate the typical data obtained at different intensities of the incident light and Tables VI and VII summarise all the data at different concentrations of the acid and bromine.

TABLE II.

Tartaric acid—M/7·5. Bromine—N/30. Temperature—33°.

Intensity of incident light—2½ Hefners-at-100 cm.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	12·55 c.c.	—	
15	12·3	—	15 minutes.
39	10·3	·00321	
67	9·1	·00252	
106	7·55	·00230	
147	6·15	·00228	

On repeating the above experiment in presence of a trace of iodine the induction period rose to 30 mins. and the velocity constant fell slightly.

TABLE III.

Tartaric acid M/7·5. Bromine—N/40. Temp.—33·2°.

Intensity of incident light—10 Hefners-at-100 cm.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	9·15 c.c.	—	
10·5	7·9	·00608	
30	6·0	·00610	Nil.
70	3·9	·00529	

TABLE IV.

Tartaric acid—M/3. Bromine—N/50. Temperature—33·2°.

Intensity of incident light—31 Hefners-at-100 cm.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	7·95 c.c.	—	
5	7·65	—	
13	5·0	·0231	4 Minutes.
23	3·15	·0214	
40	1·3	·0220	

TABLE V.

Intensity of incident light—72 Hefners-at-100 cm.

Tartaric acid—M/24. Bromine N/50. Temperature—33·8°.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	7·65	—	
5·5	6·15	·0172	
10	5·3	·0159	
19	4·3	·0132	Nil.
28	3·5	·0121	
43	2·55	·0111	

It will be seen that in all the above experiments (*vide* Tables II & V), except at relatively very high concentration of tartaric acid (*vide* Table IV) where it remains fairly constant, the unimolecular constant gradually tends to diminish. This phenomenon we have found throughout our experiments and we intend to deal with this point in a subsequent paper.

TABLE VI.

Intensity of incident light—31 Hefners-at-100 cm.—(same as in Table IV.) Temp.—33·3°.

Conc. of tartaric acid.	Conc. of bromine.	Induction period.	Limits of unimolecular constant.	Mean constant.
M/24	N/100	1½ mins.	·0200—·0173	·0183
M/15	,,	2½ mins.	·0262—·0235	·0252
M/3	,,	4 mins.	·0558—·0540	·0549
M	,,	3 mins.	·154—·151	·153
M/24	N/50	1½ mins.	·0073—·0061	·0069
M/15	,,	2½ mins.	·0101—·0080	·0088
M/3	,,	4 mins.	·023—·021	·022
M	,,	17 mins.	·052—·046	·048
M/15	N/30	2½ mins.	·00618—·00443	·0056
M/3	,,	4 mins.	·0143—·0110	·0126
M	,,	14 mins.	·0243—·0239	·0241
M/3	N/20	Nil	·0069—·0060	·0062
M	,,	12 mins.	·0143—·0128	·0134
M/3	N/10	Nil	·0034—·0025	·0030
M	,,	13 mins.	·0052—·0046	·0050

TABLE VII.

Intensity of incident light—72 Hefners-at-100 cm. (same as in Table V). Temp.—33·6°.

Conc. of tartaric acid.	Conc. of bromine.	Induction period.	Limits of unimolecular constant.	Mean constant.
M/24	N/50	Nil	·0172—·0111	·014
M/15	,,	Nil	·0246—·0183	·018
M/8	,,	Nil	·0425—·0403	·0420
*M	,,	6 mins.	·146—·141	·144
M/15	N/30	Nil	·0108—·0064	·0084
M/8	,,	Nil	·0232—·0202	·0218
*M	,,	6 mins.	·0386—·0346	·0368
M/8	N/20	Nil	·0187—·0121	·0160
*M	,,	4 mins.	·0247—·0211	·0230
M/8	N/10	Nil	·0108—·00501	·0087
*M	,,	2 mins.	·00944—·0088	·0090

Period of Induction.

It will be seen from above that the period of induction varies from 20 mins. to nil. For the same concentration of bromine an increase in the concentration of tartaric acid increases the period of induction. An increase in the concentration of bromine at the same concentration of tartaric acid slightly diminishes the induction period—as will be clear from data marked with asterisks (*) in Tables VI and VII. An increase in the intensity of light also diminishes the period of induction.

Another fact, which appears rather puzzling and which will be discussed later, is the influence of the initial concentration of bromine on the unimolecular constant. It will be at once clear from the data given in Tables VI and VII that concentration of tartaric acid remaining the same, unimolecular velocity constants diminished considerably as the initial bromine concentration increased.

Experiments at various Wavelengths.

We next carried out the reaction at various wavelengths using different solutions as filters. A bromine filter was tried first and then the different filters recommended by Plotnikow were used. Table VIII summarises the results.

TABLE VIII.

Tartaric acid—M/7·5. Bromine—N/30. Temp.—33·6°.

Filters.	Wavelength limit.	Schwerpunkt.	Intensity: Hefners-at-100 cm.	Period of induction.	Limits of unimolecular const.	Mean const.
·3N Bromine (1 cm.) & N/20 $CuSO_4$ (1 cm.)			19	45 mins.	·00202—·0016	·0018
The same			52	20 ,,	·0035—·0023	·0030
Methyl violet & potassium chromate.	718-639 $\mu\mu$	665·9 $\mu\mu$	75	30 ,,	·00136—·00130	·00133
$KMnO_4$, K_2CrO_4 & $NiSO_4$	614-576 $\mu\mu$	591·9 $\mu\mu$	8·5	90 ,,	·0015—·0013	·0014
$CuCl_2$ & K_2CrO_4	540-505 $\mu\mu$	533 $\mu\mu$	3·5	30 ,,	·00198—·00150	·0018
$CuSO_4$ & Methyl green	526-494-458 $\mu\mu$	488·5 $\mu\mu$	11·5	Nil	·0110—·0059	·0089
Methyl violet & $CuSO_4$	478-410 $\mu\mu$	488 $\mu\mu$	3·8	Nil	·0054—·0031	·0048

The last two filters, therefore, corresponding to the blue and deep blue regions are the most and almost equally efficient photo-chemically. Absorption measurements with a Johansen thermopile behind the reaction cell filled with water and N/30 bromine solution showed that the reaction mixture (1 cm. thick) absorbed about 18% of the radiation 488·5 $\mu\mu$ and 448 $\mu\mu$ and 2 % of 533$\mu\mu$ while it showed very little absorption at other regions.

It will be seen that for blue and violet light of wavelengths shorter than 500 $\mu\mu$ even for weak intensities of light the period of inductions is approximately zero and the velocity of reaction is very

large compared with the corresponding value for lights of very much higher intensity at larger wavelengths.

It will be seen from the previous observations that the reaction in blue light is characterised by greater simplicity and we shall now describe the results of our experiments in blue light (488·5 $\mu\mu$) and the effect of various addition agents on the reaction.

Tables IX, X, XI give the typical results while Table XII summaries the results of the reaction in blue light.

TABLE IX.

Intensity of incident light (488·5 $\mu\mu$)—6 Hefners-at-100 cm.

Tartaric acid—M/3. Bromine—N/30. Temp.—33·5°.

Time in mins.	N/200 Bromine.	Unimolecular const.	Period of induction.
0	12·55 c.c.	—	
8	11·2	—	4 minutes.
16	9·15	·0110	
46	5·5	·0081	
76	3·2	·0080	

TABLE X.

Intensity of incident light (488·5 $\mu\mu$)—6 Hefners-at-100 cm.

Tartaric acid—M. Bromine—N/30. Temp.—33·6°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	13·0 c.c.	—	
	12·7	—	5 minute
10	10·55	·0161	
16	8·9	·0140	
41	3·7	0147	

TABLE XI.

Intensity of incident radiation (488·5 $\mu\mu$) – 2 Hefners-at-100 cm.

Tartaric acid – M/7·5. Bromine – N/30. Temp. – 33·6°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	13·1 c.c.	—	
30	12·9	—	35 minutes
60	11·4	—	
90	9·7	·00234	
141	7·6	·00218	
201	5·6	·00219	

As in the case of experiments in white light the unimolecular constant, except in the case of relatively higher concentration of tartaric acid, has a tendency to diminish. This tendency is more marked at higher intensities of incident light. The induction period rapidly increases as the intensity of incident radiation diminishes.

TABLE XII.

Temperature – 33·5°.

Conc. of tartaric acid.	Conc. of bromine.	Intensity of blue light (Hefners-at-100 cm.).	Period of induction.	Limits of unimolecular constant.	Mean constant.
M/7·5	N/30	11·5	Nil	·0110 – ·0059	·0089
M/15	,,	6	Nil	·0047 – ·0032	·0042
M/3	,,	6	4 mins.	·0110 – ·0080	·0095
M	,,	6	5 mins.	·0161 – ·0136	·0150
M/3	N/20 (·96)	6	Nil	·00610 – ·0051	·0054
M/3	N/50	6	4 mins.	·0202 – ·0183	·0190
M/3	N/75	6	5 mins.	·049 – ·051	·050
M/7·5	N/30	2	35 mins.	·00234 – ·0021	·0023
M/15	N/30	2	20 mins.	·00174 – ·00171	·00173

As before the induction period increases with increase in concentration of tartaric acid and diminishes with the increase in concentration of bromine and intensity of incident light. The constant of unimolecular reaction increases with increase in concentration of tartaric acid but diminishes considerably as the initial concentration of bromine is increased.

Determination of the Temperature Coefficient in Blue Light.

Table XIII shows that the temperature coefficient of the reaction in blue light is 2.

TABLE XIII.

Intensity of incident light (488·5 $\mu\mu$)—5·8 Hefners-at-100 cm.

Temp.	Conc. of Br.	Conc. of tartaric acid.	Limits of unimolecular constants.	Mean const.	Period of induction.
24°	N/30 (1·1)	M/3	·00404—·00336	·00380	10 mins.
34°	N/30 (1·1)	M/3	·00881—·00663	·00760	5 mins.

The temperature co-efficient of the dark reaction is, as has already been mentioned, 4·6.

Application of Einstein's Law.

The quantum efficiency of the reaction can throw some light on its mechanism. We shall, therefore, find out the relation between the number of quanta absorbed and the number of molecules reacting.

Absorption measurements, as has already been mentioned, with a Johansen thermopile showed that a N/30 aqueous solution of bromine, 1 cm. thick, absorbed only 18% of the incident blue light (488·5 $\mu\mu$) transmitted by filters recommended by Plotnikow. Measurements of extinction coefficient of bromine solutions with a spectro-photometer, however, showed that a 1 cm. layer of N/30 bromine solution should absorb 80% of incident blue light. From this it is evident that Plotnikow's filters are imperfect.

We shall take the results in Table IX. Taking Gerlach's value of 900 ergs. per sq. cm. per second at a distance of 1 metre for the energy emitted by a Hefner lamp and remembering that only 18%

of the incident light was absorbed we have the number of quanta absorbed

$$= 900 \times 6 \times \frac{18}{100} \times \frac{1}{6{\cdot}5 \times 10^{-27}} \times \frac{488{\cdot}5 \times 10^{-7}}{3 \times 10^{10}}$$

$$= 243{\cdot}5 \times 10^{19} \text{ quanta per sq. cm. per second.}$$

Since in 8 mins. the change in 2 c.c. of reaction mixture is (11·2—9·15) 2·05 c.c. of N/200 bromine after the induction period is over, the number of molecules transformed per sq. cm. per second

$$= \frac{2{\cdot}05}{2 \times 2 \times 2 \times 100} \times {\cdot}001 \times \frac{1}{8 \times 60} \times 6{\cdot}1 \times 10^{23}$$

$$= 325{\cdot}600 \times 10^{18} \text{ molecules per sq. cm. per second.}$$

Thus for one quantum of light (488·5 $\mu\mu$) absorbed, about 13 molecules disappear.

Table XIV summarises the quantum efficiency under different concentrations of tartaric acid, the intensity of the incident blue light being in all cases 6 Hefners-at-100 cm.

TABLE XIV.

Conc. of tartaric acid.	Conc. of bromine.	No. of Br. molecules transformed per quantum.	Remarks.
M/3	N/75	58	After the period of induction.
M	N/30	23	After the period of induction.
M/3	N/30	13	After the period of induction.
M/7·5	N/30	17	No period of induction.
M/15	N/30	6	No period of induction.

The quantum efficiency is thus large.

Experiments in Presence of Sodium Hydrogen Tartrate.—The photo-chemical reaction between bromine and tartaric acid was carried out in presence of Na-H-tartrate at a constant concentration. The object was to find out how an increase in the concentration of hydrogen tartrate ion which we shall always indicate by HT' and a

change in the initial p_H would affect the velocity of reaction and the induction period.

It was first found out that the dark reaction between bromine, tartaric acid and sodium hydrogen tartrate was negligible at 32°—with a sodium hydrogen tartrate concentration of M/15, tartaric acid concentration of M/15 and bromine concentration of N/30, the velocity constant fell gradually from ·00059 to ·00024.

p_H values for the mixtures of NaH-tartrate and tartaric acid were determined by the potentiometric method.

Tables XV, XVI, XVII, XVIII indicate the typical reaction in blue light and Tables XIX and XX summarise the data.

TABLE XV.

Intensity of incident light (488·5 $\mu\mu$)—3·84 Hefners-at-100 cm.

NaH-tartrate—M/30
Tartaric acid—M/30
} M/15 ; p_H =2·71.

Bromine.—N/30. Temp.—33·5°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	12·9 c.c.	—	Nil
5	10·15	·0208	
20	6·0	·0166	
30	4·25	·0161	
42	2·8	·0158	

TABLE XVI.

Intensity of incident light (488·5 $\mu\mu$)—3·84 Hefners-at-100 cm.

NaH-tartrate—M/30
Tartaric acid—29/30 M
} M; p_H =1·4

Bromine.—N/30. Temp.—33·5°.

Time in mins.	N/200 Bromine.	Constant.	Period of induction.
0	13·1 c.c.	—	Nil
6	8·25	·0335	
11	6·2	·0295	
16	4·25	·0306	

Table XVII.

Intensity of incident light (488·5 $\mu\mu$)—1·3 Hefners-at-100 cm.

NaH-tartrate—M/30
Tartaric acid—M/10 } M/7·5; p_H −2·4

Bromine—N/30. Temp.—33·5°.

Time in mins.	N/200 Bromine.	Constant.	Period of induction.
0	13·25 c.c.	—	3 minutes.
10	10·9	—	
20	7·3	·0174	
30	6·6	·0109	
40	5·2	·0107	
55	3·8	·0101	

Table XVIII.

Intensity of incident light (488·5 $\mu\mu$)—1·3 Hefners-at-100 cm.

NaH-tartrate—M/30
Tartaric acid—3M/10 } M/3; p_H −1·9.

Bromine—N/30. Temp.—33·5°.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	12·7 c.c.	—	7 minutes.
7	11·45	—	
12	9·9	·0126	
19	7·8	·0189	
27	6·35	·0128	
37	4·6	·0132	

TABLE XIX.

Intensity of incident light (488·5 $\mu\mu$)—3·84 Hefners-at-100 cm.

Conc. of NaH-tartrate—M/30. Temp.—33·5°.

Conc. of tartaric acid.	Sum of conc. of NaH — tartrate and tartaric acid.	Conc. of Br.	p_H	Induction period.	Limits of constants.	Mean constant.
M/30	M/15	N/30	2·71	Nil	·0208—·0158	·0184
M/10	M/7·5	,,	2·4	Nil	·0263—·0161	·0217
3M/10	M/3	,,	1·9	Nil	·0286—·0217	·0267
29M/30	M	,,	1·4	Nil	·0335—·0295	·031
M/10	M/7·5	N/50	2·4	Nil	·0411—·0353	·0385
M/10	M/7·5	N/20	2·4	Nil	·0194—·0122	·0163

TABLE XX.

Intensity of incident radiation (488·5 $\mu\mu$)—1·3 Hefners-at-100 cm.

Conc. of NaH-tartrate M/30. Temp.—33·5°.

Conc. of tartaric acid.	Sum of conc. of Na-H— tartrate and tartaric acid.	Conc. of Br.	p_H	Induction period.	Limits of constant.	Mean const.
M/10	M/7·5	N/30	2·4	4 mins	·0174—·0101	·0140
M/10	M/7·5	N/50	2·4	4 ,,	·0285—·0192	·0245
3M/10	M/3	N/30	1·9	7 ,,	·0139—·0126	·0134
29M/30	M	N/30	1·4	17 ,,	·0168—·0164	·0165

It will be seen by comparing the above data with those in absence of NaH-tartrate given in Table XII that the presence of NaH-tartrate greatly accelerates the reaction and diminishes the period of induction. Again from Table XX it will appear that keeping the initial bromine concentration constant at N/30, if the p_H value of the solution is diminished, *i.e.*, the concentration of hydrogen ion is increased, the induction period for weak light (1·3 Hefners) increases. It should be noticed also that the unimolecular constant simultaneously increases.

It will also appear from Table XXI, where the ratios of the velocity constants are compared with intensity ratios, that the ratios of the

corresponding velocity constants is equal to the ratio of the square root of the intensities of incident radiation.

TABLE XXI.

Conc. of NaH-tartrate— M/30 throughout.

Conc. of tartaric acid.	Sum of conc. of NaH-tartrate and tartaric acid.	Conc. of bromine.	Ratio of square root of intensities.	Ratio of velocity constants.
M/10	M/7·5	N/30	$\sqrt{\frac{3·84}{1·3}}=1·7$	$\frac{·0217}{·0140}=1·6$
3M/10	M/3	,,	1·7	$\frac{·0267}{·0134}=2·0$
29M/30	M	,,	1·7	$\frac{·0310}{·0165}=1·9$
M/10	M/7·5	N/50	1·7	$\frac{·0385}{·0245}=1·6$
				Mean — 1·85

Effect of Hydrobromic Acid.

Since HBr is one of the products of reaction it was thought advisable to note its effect on the reaction. It was also felt that since p_H has a large influence on the period of induction as just noted, addition of HBr to the reaction mixture previous to exposure to light might furnish a clue as to the mechanism of induction period.

Tables XXII, XXIII, XXIV give the typical data while Table XXV summarises all the observations.

TABLE XXII.

Intensity of light (488·5$\mu\mu$)—11·5 Hefners-at-100 cm.

Tartaric acid—M/3. Bromine—N/30. Initial conc. of HBr—Zero.

Temp.—33·3°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Induction period.
0	12·9 c.c.	—	Nil
5	10·7	·0162	
15	7·9	·0142	
26	6·2	·0122	
39	4·55	·0116	
56	3·15	·0109	

TABLE XXIII.

HBr—N/200 ; other conditions same as in Table XXII.

Time in mins.	N/200 Bromine.	Constant.	Period of induction.
0	13·1 c.c.	—	2 minutes
5	12·15	—	
16	9·7	·00889	
26	8·1	·00838	
46	5·6	·00820	
64	4·2	·00782	

TABLE XXIV.

HBr— N/100 ; other conditions same as in Table XXII.

Time in mins.	N/200 Bromine.	Const.	Period of induction.
0	13·05 c.c.	—	17 minutes.
5	12·5	—	
15	11·15	—	
30	8·8	·00685	
45	6·7	·00737	
60	5·2	·00787	

TABLE XXV.

Intensity of light (488·5$\mu\mu$)—11·5 Hefners-at-100 cm.

Tartaric acid— M/3. Bromine—N/30. Temp.—33·3°.

Initial conc. of HBr.	Period of induction.	Limits of unimolecular constant.	Mean constant.
Nil	Nil	·016—·0109	·0140
N/200	2 mins.	·00889—·00782	·0083
N/150	3 mins.	·00845—·00779	·0080
N/100	17 mins.	·00737—·00685	·0072
N/75	22 mins.	·00687—·00635	·0066
N/50	35 mins.	·00598—·00552	·00575

It will thus transpire from the foregoing results that addition of HBr diminishes the velocity of the reaction but increases considerably the period of induction. It also introduces an induction period where there was none. The effect increases with inceasing concentration of the HBr added initially. It will also be seen from above data that if no HBr be added initially, although there is no induction period, the velocity constants diminish very rapidly (*vide* Table XXII). If, however, we add some HBr to start with, the period of induction, the duration of which is proportional to the amount of HBr added, makes its appearance but the velocity constants do not diminish so rapidly. Such results are indeed to be expected. In the absence of any HBr, as the reaction proceeds, HBr is generated and gives rise to H^+ ions the concentration of which thus changes considerably relatively to the initial concentration. As we have already seen H^+ ions act retardingly on the reaction and thus greatly diminish the velocity of reaction. If, however, HBr be added initially, the relative increase in the concentration of H^+ ion is not considerable and therefore the retarding influence on the velocity of the reaction does not increase to very great extent. In presence of HBr, the duration of the induction period should, therefore, be proportional to the concentration of HBr added and the velocity constants should not diminish as rapidly as in its absence.

The experiments in presence of HBr thus throw a good deal of light on the mechanism of the reaction and we intend to discuss it more thoroughly in a subsequent paper.

Photochemical After-effect.—We have investigated more fully the after-effect exhibited by this reaction. The reaction mixture was first exposed for short periods to intense parallel radiation from 1000 c.p. point-o-lite lamp using $CuSO_4$ and KNO_3 filters and then quickly transferred to darkness. The after-effect persisted for about half-an-hour. Table XXVI indicates the typical result and Table XXVII summarises the observations. The constants have been calculated in the same way as in Part I. The intensity of the radiation was 72 Hefners-at-100 cm., concentration of tartaric acid M/3 and that of bromine N/30. Temperature was maintained at 32°.

TABLE XXVI.

Time in mins.	N/200 Bromine.	Unimolecular constants for after-effect.
0	13·5 c.c.	
After illumination for 5 mins. kept in the dark and then		
0	9·7	
5½	9·0	·0425
15	8·5	·0354
25	8·2	·0372
	Final 8·0	

Time of exposure in mins.	Limits of const. for after-effect.	Mean const. for after-effect.	Unimolecular const. for the light reaction under same conditions.
5	·0425—·0354	·0385	
8	·0396—·0331	·0365	·0218
16	·0526—·0417	·0422	
25	·0451—·0359	·0400	

It will be seen that the velocity coefficient for the after-effect is of the same order as obtained in Part I and does not depend on the period for which the system is illuminated before it is removed to darkness.

Reactions in Red Light.—We tried to find out if the addition of a blue substance like $CuSO_4$ to the reaction mixture would make the reaction proceed quickly in red light which is practically not absorbed at all by bromine solutions. For this purpose the reaction without any $CuSO_4$ was first carried out in red light obtained by using methyl violet and potassium chromate filters. The reaction in red light shows a very large period of induction and then proceeds very slowly. Table XXVIII gives only a few of our observations.

TABLE XXVIII.

Intensity of incident radiation (665·9$\mu\mu$)—68 Hefners-at-100 cm.

Temp.—33.7°.

Conc. of tartaric acid.	Conc. of bromine.	Induction period.	Limits of unimolecular constant.	Mean constant.
M/15	N/30	50 mins.	·0012—·00099	·0010
M/3	,,	100 ,,	·00201—·00185	·00192
M/3	N/75	210 ,,	·0070—·0066	·0068

The addition of $CuSO_4$ in all cases increased the induction period and diminished the velocity constants.

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On Photochemical Reaction between Bromine and Tartaric Acid in Aqueous Solutions. Part III. The Mechanism of the Reaction.

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Any mechanism that may be postulated for this photochemical reaction should account for the following experimental observations recorded in Part II (*previous paper*).

1. The induction period diminishes with increase in the frequency and intensity of incident light.

2. The induction period increases as the initial concentration of tartaric acid increases.

3. The induction period diminishes as the initial concentration of bromine is increased.

4. The induction period increases very considerably if hydrobromic acid is added to the reaction mixture previous to exposure to light.

5. In a reaction mixture containing bromine, tartaric acid and sodium hydrogen tartrate, the induction period increases as the initial p_H of the solution diminishes.

6. The unimolecular velocity constant with respect to bromine, diminishes as the initial concentration of bromine increases.

7. The same constant increases as the concentration of tartaric acid increases.

8. The value of this constant increases very considerably if a fraction of the tartaric acid in the reaction mixture is replaced by an equivalent amount of sodium hydrogen tartrate.

9. The value of this constant diminishes considerably if hydrobromic acid is added to the reaction mixture before exposure to light.

10. As the reaction proceeds, the unimolecular constant with respect to bromine continues to diminish, this diminution being more marked in weaker solutions of tartaric acid than in the more concentrated solutions. In a mixture of bromine with excess of tartaric acid and sodium hydrogen tartrate the values of the unimolecular constant are fairly concordant among themselves.

11. The velocity of the reaction increases very rapidly as the frequency and the intensity of light increases. In fact for blue light,

in a mixture of bromine with excess of tartaric acid and sodium hydrogen tartrate, the values of the unimolecular constant vary approximately as the square root of light intensity.

12. A quantum of light absorbed by the system is responsible for the transformation of a large number of bromine molecules into hydrobromic acid.

It appears that all these complex features of the reaction between bromine and tartaric acid in aqueous solution can be explained if we assume the following mechanism of reaction:—

The first stage in the reaction is obviously the activation of bromine molecules by the absorption of light. The experiments of Bodenstein and Berthoud, and the various experiments on photobromination carried out in this laboratory indicate that it is the atom of bromine that is responsible for bringing about photochemical reaction. This hypothesis has been corroborated by the work of Frank who has shown that a quantum of wave-lengths shorter than the band limit of bromine, *i.e.*, 5200Å, decomposes the bromine molecule into a normal atom and a metastable atom (Faraday. Soc. Discussion on "Photo-chemical Reactions in Liquids and Gases", p. 540). We assume necessarily the following transformation:—

$$Br_2 + h\nu \text{ (where } \frac{1}{\nu} < 5200\text{Å}) \longrightarrow 2\,Br \quad \ldots \quad \ldots \quad (1)$$

We have seen, however, that green, yellow and even red light is in a position to bring about photobromination, though the efficiency of light diminishes very rapidly as the wave-length increases. It is well known that the absorption for moist bromine vapour begins at 6100Å, and for bromine solution it begins somewhat earlier. But quantum of this frequency is not in a position to decompose bromine molecules, which are only pushed up to a certain stage of activation. These activated molecules may, in some cases, acquire fresh energy by collision with other molecules in the system, and undergo dissociation into atoms. This possibility of the transformation of the kinetic energy of collision into the heat of dissociation of bromine is the greater, the greater the internal energy of preliminary activation of the bromine molecule by the absorption of a quantum of radiation. It is well known that this possibility of conversion of energy of collision into internal energy of active molecules is the real reason for the absence of a photochemical threshold which we

meet with in simple photo-electric phenomena. It therefore follows that absorption of light where γ is greater than 5200Å may lead to the dissociation of bromine molecules into atoms, but the fraction of excited molecules so dissociated into atoms rapidly diminishes as the wave-length increases. We have thus a qualitative explanation of the observed fact that the efficiency of light for photobromination diminishes rapidly as the wave-length increases beyond 5200Å.

We should next trace the various phases through which this bromine atom passes. In the first place two atoms of bromine may combine to regenerate a molecule of bromine thus

$$2Br \longrightarrow Br_2$$

The rate of re-formation of bromine molecule is therefore

$$K_2[Br]^2 \quad \ldots \quad \ldots \quad (2)$$

Secondly, an atom of bromine is deactivated by collision with molecules of oxygen present in the system.

$$\left.\begin{aligned} Br + O_2 &\longrightarrow BrO_2 \\ BrO_2 + Br &\longrightarrow Br_2 + O_2 \end{aligned}\right\} \quad \ldots \quad \ldots \quad (3)$$

This theory is very familar to all investigators who have studied photochemical reactions in which chlorine or bromine is involved. It has always been found that the presence of oxygen very considerably retards the velocity of reaction and the current explanation is that whenever an atom of chlorine or bromine collides with a molecule of oxygen, it becomes practically inert for purposes of photo-halogenation.

The rate of deactivation of bromine atom is, from (3), given by

$$K_3[Br]^2[O_2] \quad \ldots \quad \ldots \quad (4)$$

where $[O_2]$ represents the concentration of oxygen molecules in the system. The presence of oxygen can be traced to two sources.

(1) Oxygen remaining dissolved in water used for these experiments.

(2) Oxygen obtained from the dark reaction,

$$Br_2 + H_2O \longrightarrow 2HBr + O$$

The velocity of this dark reaction, as has been noted already is very small and falls off with time, and perhaps in a closed vessel, we are dealing with reversible reaction of the type,

$$2Br_2+2H_2O \rightleftharpoons 4HBr+O_2 \qquad \ldots \quad (5)$$

Since the velocity of reactions indicated in (5) is very small, equilibrium concentration of oxygen, once attained, will not be perceptibly disturbed if the concentration of bromine rapidly diminishes or the concentration of hydrobromic acid quickly increases in the course of another rapid side reaction.

The concentration of oxygen in the reaction mixture may thus be considered constant during the processes of photobromination which in our experiments were completed in about three hours.

This equilibrium condition of oxygen existing in the solution previous to the exposure to light is from (5) obviously proportional to the square of the initial concentration of bromine;

$$\text{or} \quad [O_2]=K_4\,[Br_2]^2 \text{ initial} \qquad (6)$$

Thirdly, in the initial stage of photobromination, the active bromine atoms may be used up in destroying a class of substances which act as photo-inhibitors and which are almost invariably present in reacting systems. This inhibition effect is very pronounced in the photochemical reaction between hydrogen and chlorine. Thus Weigert (*Zeit. physikal. Chem.*, 1928, **131**, 271) recommends the following precaution in the preparation of Bunsen—Roscoe actinometer:—

"Zunächst wurde nach jeder Neufüllung des Aklinometers das Gas-gemisch mit einer kleinen Glühlampe, die mit 0·6 Amp. und 6 Volt an einer Akkumulatorenbatterie Konstant brannte, induziert. Wenn das Gas einige Tage und Nächte ununterbrochen durch das system hindurchgeleitet war, war die Induktionsperiode schnell überwunden, und man erhielt immer wider Indexbewegungen derselben Grössenordnung von etwa 2 cm./Min bei einem Abstand der Prüflampe vou 1 m."

The rate of destruction of these photo-inhibitors will therefore be proportional to the concentration of bromine, and the intensity of incident radiation. Here too, the frequency of light exerts a great effect, for the higher the frequency, the greater is the possibility of

the decomposition of the bromine molecules into active atoms, and hence, the quicker is the rate of destruction of inhibitors.

It appears that hydroxyl ions have also great influence on the rate of destruction of these inhibitors by bromine in presence of light. Chlorine and bromine in an aqueous solution containing (OH') ions give the hypochlorite and the hypobromite respectively. In the case of sodium hypochlorite solution, it has been definitely shown by W. C. McLewis, (*J. Chem. Soc.*, 1912, **101**, 237) that the hypochlorite decomposes in light in alkaline or neutral solution into sodium chloride and atomic oxygen. The rate of production of atomic oxygen is proportional to the concentration of hypochlorite ion and the intensity of blue and violet radiation. The active rays are in the blue, violet and ultraviolet regions. In the dark, however, the decomposition takes place only very slowly. Similarly to chlorine, we may assume that bromine produces hypobromite by reaction with hydroxyl ions, and this hypobromite ion in presence of blue and violet light decomposes into bromide ion and an atom of oxygen. The photo-inhibitors present in the reacting system is very quickly destroyed by the atom of oxygen and transformed into harmless substances. On this basis, is readily intelligible the influence of the following factors on the diminution of induction period :—

(1) Increase in the intensity of illumination.
(2) Increase in the frequency of radiation.
(3) Increase in concentration of bromine.
(4) Increase in the concentration of OH' ion.

Lastly, the active bromine atoms are responsible for the photo-bromination of tartaric acid. We have seen that one quantum of absorbed radiation can transform more than 50 bromine molecules. This is possible, if we have a chain mechanism in which the bromine atom used up in a reaction, is regenerated in a subsequent reaction. Such chain reactions are, however, bound to be hypothetical unless in any instance, the intermediate compounds postulated in such mechanism can be proved to exist. It is preferable to imagine that in the bromination of tartaric acid which is an exothermal reaction, the bromine atoms are not actually used up and regenerated in alternate chains, but that the bromination can only take place in a three-body collision, between a bromine atom, a bromine molecule, and a bitartarate ion : the bromine atom may be considered to be a catalyst which remains unaltered during this transformation.

The rate of photo-bromination will then be given by

$$-\frac{d[Br_2]}{dt}=K[Br]\,[Br_2]\,[HT'] \qquad \ldots (7)$$

We have postulated above that it is the HT′ which takes part in photobromination and not the molecule of tartaric acid, There are two reasons for this assumption—

(*a*) If the reaction mechanism as given by (7) were modified so as to substitute a molecule of tartaric acid in place of (HT′) ion, the reaction, for a constant concentration of bromine atom after a stationary state has been reached, would have been bimolecular. The bimolecular velocity constants were however not found concordant among themselves.

(*b*) It has been mentioned before that if the total initial concentration of tartrate radical be kept constant in a reaction mixture but the ratio of HT′ to tartaric acid molecule increased by taking suitable proportions of sodium hydrogen tartrate and tartaric acid, then the reaction velocity increases very considerably. This observation is thus a definite evidence in favour of the assumption that HT′ ion and not the molecule of tartaric acid is the reactive substance. Equation (7) is capable of quantitative verification from the experimental data recorded in the previous paper.

The concentration of free [Br] after a stationary state has been reached and the photo-inhibitors destroyed, can be obtained from the equation,

$$\frac{d[Br]}{dt}=K_1I-K_2[Br]^2-K_3[Br]^2[O_2]=0$$

$$\text{or } [Br]=\sqrt{\frac{K_1 I}{K_2+K_3[O_2]}}$$

$$=\sqrt{\frac{K_1 I}{K_2+K_3.K_4[Br_2{}_{\text{initial}}]^2}} \qquad \ldots (8)$$

where I is the intensity of incident light and K_1I, therefore, represents the rate at which the free [Br] is generated. This is true only under the condition that the value of I absorbed does not vary during the progress of the reaction. In a paper by Ghosh and Purkayastha, (This *Journal*, 1927 **4**, 420,) this point has been thoroughly discussed and it has been shown that for blue light the variation in the amount of light absorbed during the progress of the

reaction when the final bromine concentration drops to a quarter of its initial value is negligible. The rate of disappearance of bromine is equivalent to the rate of formation of HBr and we have

$$\frac{d[\mathrm{HBr}]}{dt}$$

$$\text{or } \frac{dx}{dt}=K(a-x).\ [\mathrm{HT'}]\left\{\sqrt{\frac{K_1 I}{K_2+K_3K_4[\mathrm{Br_2\ initial}]^3}}\right\}\ldots \quad (9)$$

The term within { } may be considered constant during the progress of a reaction, and we have

$$\frac{dx}{dt}=K(a-x)[\mathrm{HT'}].K_5 \qquad \ldots \quad (10)$$

The concentration of HT′ in a solution of tartaric acid is given by the Ostwald equation,

$$[\mathrm{H^+}]\ [\mathrm{HT'}]=K_6[\text{tartaric acid}]$$

where K_6 is the first dissociation constant of tartaric acid. Now C, the concentration of tartaric acid may be taken as constant during a reaction because (1) K_6 is very small, *i.e.*, practically the whole of the acid may be considered as undissociated and (2) the concentration of tartaric acid in our experiments was always far in excess of that of bromine, the ratio of molecular concentration of tartaric acid to bromine being never less than 8.

Now at any stage of the reaction when the concentration of hydrobromic acid is x, x', the conc. of HT′ ion is given by

$$(x+x')(x')=K_6C$$

$$\text{or, } x'=\frac{-x+\sqrt{x^2+4K_6C}}{2}$$

The velocity of reaction is therefore given by

$$\frac{dx}{dt}=K.K_5(a-x)\left\{\frac{-x+\sqrt{x^2+4K_6C}}{2}\right\} \qquad \ldots \quad (11)$$

Where a is the initial concentration of bromine in gram equivalents per litre, x is the amount of bromine in gram equivalents that disappeared at any time t, C is the molecular concentration of tartaric acid in gram molecule per litre, K_e is Ostwald's constant for the first dissociation of tartaric acid when concentration is expressed in gram molecule per litre (0·00099).

The integration of the equation (11) is rather complicated but it can be accomplished and we obtain the relation

$$2(K_eC).\ K.K_st = \text{Constant} - (x + \sqrt{x^2+4K_eC})$$

$$-(a+\sqrt{a^2+4K_e})C\ \log(a-x)\ -a\log e(x+\sqrt{x^2+4K_eC})$$

$$+(\sqrt{a^2+4C}\log e\,(\sqrt{a^2+4K_eC})\sqrt{x^2+4K_eC})$$

$$+ax+4K_eC) \qquad \ldots\ (12)$$

The expression to the left will in the following table be designated by A.

In Table I, are given some experimental data which go to show that the constants obtained from equation (12) agree very well among themselves: t is expressed in minutes.

Table I (*vide* Table VIII—Part II).

Filters of copper sulphate and methyl violet solutions were used as recommended by Plotnikow to obtain light of wave-lengths between 4780—4100Å (Schwerpunkt—4480Å).

Intensity—3·8 Hefners-at-100 cm.

Initial conc. of tartaric acid—M/7·5. Initial conc. of bromine N/30.

Temp.—33·6°.

t	$a-x$	x	A	$K.K_s$	Unimolecular velocity constant with respect to $[Br_2]$.
0	·03425	0	2·3 × ·0402	—	—
20	·02675	·0075	2·3 × ·0430	1·21	·0054
45	·02190	·0125	2·3 × ·0460	1·20	·0043
101	·01500	·0191	2·3 × ·0534	1·20	·0035
191	·00875	·0255	2·3 × ·0663	1·21	·0031

Tables II-VI give some typical data for light of wave-length 526-458$\mu\mu$ (Schwerpunkt 488·5$\mu\mu$) and it is at once evident that the constants obtained from equation (12) agree very well amongst themselves.

TABLE II (*vide* TABLE XXII, PART II).

Intensity of incident light (488·5$\mu\mu$)—11·5 Hefners-at-100 cm. Tartaric acid—M/3. Bromine N/30. Temp.—33·3°.

t	$a-x$	x	A	KK_s	Unimolecular constant.
0	·03225	0	2·3 × ·02910	—	—
5	·02675	·00550	2·3 × ·03234	2·23	·0162
15	·01975	·01250	2·3 × ·03837	2·13	·0142
26	·01550	·01675	2·3 × ·04422	2·01	·0122
39	·01137	·02086	2·3 × ·05218	2·04	·0116
56	·00787	·02438	2·3 × ·0682	2·08	·0109

TABLE III.

Intensity of incident light (488·5$\mu\mu$)—11·5 Hefners-at-100 cm. Tartaric acid—M/7·5. Bromine—N/30. Temp.—33·5°.

t	$a-x$	x	A	KK_s	Unimolecular constant.
0	·03400	0	2·3 × ·04093	—	—
25	·02075	·01325	2·3 × ·04762	2·31	·0086
41	·01700	·01700	2·3 × ·05160	2·24	·0073
72	·01200	·02200	2·3 × ·05912	2·19	·0063
106	·00800	·02600	2·3 × ·06952	2·33	·0059

TABLE IV (*vide* TABLE XII, PART II).

Intensity of incident light (488·5$\mu\mu$)—6 Hefners-at-100 cm. Tartaric acid—M/15. Bromine—N/30. Temp.—33·5°.

t	$a-x$	x	A	KK_s	Unimolecular constant.
0	·03275	0	2·3 × ·04213	—	—
10	·029375	·003375	2·3 × ·04292	1·36	·0047
30	·024625	·008125	2·3 × ·04479	1·53	·0041
60	·02075	·01200	2·3 × ·04694	1·38	·0033
90	·01700	·01575	2·3 × ·05000	1·53	·0032

TABLE V (*vide* TABLE IX, PART II).

Intensity of incident light (488·5$\mu\mu$)—6 Hefners-at-100 cm. Tartaric acid—M/3. Bromine—N/30. Temp.—33·5°.

t	$a-x$	x	A	KK_s	Unimolecular constant.
0	·031375	0	2·3 × ·02799	—	—
8	·02800	·0338	2.3 × ·02996	—	—
16	·022875	·0085	2·3 × ·03373	1·60	·0110
46	·01375	·01763	2·3 × ·04630	1·48	·0081
76	·00800	·02338	2·3 × ·05998	1·52	·0080

TABLE VI.

Intensity of incident light (488·5$\mu\mu$)—6 Hefners-at-100 cm. Tartaric acid—M/3. Bromine—N/20. Temp.—33·5°.

t	$a-x$	x	A	KK_s	Unimolecular constant.
0	·04550	0	2·3 × ·04542	—	—
10	·03925	·00625	2·3 × ·04785	·842	·00610
25	·03300	·01250	2·3 × ·05150	·842	·00564
45	·02675	·01875	2·3 × ·05662	·856	·00513

It will be seen that the value of the constants KK_s in the fifth vertical column agree very well among themselves, whereas the unimolecular velocity constants with respect to bromine rapidly diminish as the reaction proceeds.

Table VII contains the values of constants KK_s for blue light with Schwerpunkt at 488·5 Å.

Light intensity Hefners-at-100 cm.	Initial conc. of tartaric acid.	Initial conc. of bromine.	KK_s
11·5*	M/7·5	N/30	2·25
11·5	M/3	N/30	2·10
6	M/15	N/30	1·45
6	M/3	N/30	1·55
6	M/3	N/20	·86

* The value of the intensity is only approximate.

It will be seen that when the initial concentration of bromine and the intensity of the incident light are the same, the product of the constants KK_s is, as is to be expected, independent of the concentration of tartaric acid.

Also for the same concentration of bromine, the ratio of the velocity constants ($2{\cdot}15/1{\cdot}5 = 1{\cdot}43$) is equal to the ratio of the square root of the corresponding light intensities ($\sqrt{11{\cdot}5/6}=1{\cdot}40$). This is exactly what is demanded by equation (9) for the velocity of the reaction.

With increase in the initial concentration of bromine, the product KK_s diminishes at the same intensity of incident light. This is also to be expected as the value of K_s is dependent on the initial concentration of bromine, being, as is indicated before, given by the expression,

$$K_s = \sqrt{\frac{K_1 I}{K_2 K_3 K_4 [\mathrm{Br_{2\,initial}}]^2}}$$

In fact if K_2 is small compared with $K_3 K_4 [\mathrm{Br_{2\,initial}}]^2$, we should expect that K_s should be inversely proportional to the initial concentration of bromine, which is approximately the case as will be seen from Table VII.

When the concentration of the bitartrate ion approximately remains constant during the course of the reaction, the progress of the reaction is given by the simple equation,

$$\frac{dx}{dt} = K(a-x).C.K_s \qquad \ldots \quad (13)$$

and the equation is that of a monomolecular reaction, where

$$K' = K.C.K_s = \frac{1}{t} \log \frac{a}{a-x}.$$

The value of K' is proportional (*i*) to the original concentration of the bitartrate ion and (*ii*) to the square root of the intensity of illumination. These experimental conditions are realised when to the

reaction mixture containing bromine and tartaric acid, sufficient sodium hydrogen tartrate is added. It will be seen from Tables XVI and XVIII in Part II that the unimolecular velocity constants for large concentrations of tartaric acid containing sufficient sodium hydrogen tartrate are fairly concordant among themselves, and these constants for the same initial concentration of bromine are proportional to the square root of the intensity of the incident light.

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Action of Hydrazides. Part II. Synthesis of some Bis-triazoles from Thiocarbo- and Carbo-hydrazides.

By Satish Chandra De.

In a previous paper (this *Journal*, 1927, **4**, 180) it was shown that thiocarbohydrazide condensed with phenanthraquinone and its monoxime yielding respectively a red hydrazone and a red bis-triazole derivative. In the present communication the hydrazide has been coupled with a number of derivatives of the quinone and its monoxime with a view to observe the effect of substitution in the phenanthrene ring by bromine atom and nitro group on the colour of the hydrazones and the triazoles ; and as a result it has been found that these atoms or groups have very little influence on the colour of the compounds produced.

Owing to the interesting results obtained in the foregoing cases it has been thought desirable to study the action of carbohydrazide on the various derivatives of phenanthraquinone and its monoximes and thus to draw a comparison of colour between the series of compounds which differ in having a sulphur atom in one and an oxygen atom in the other. The colour of the oxygen containing compounds are found to be mostly yellow while those of the sulphur containing compounds are red. The former are, therefore, apparently lighter in colour than the latter. The natural conclusion is that the tendency of the sulphur atom is to deepen the colour.

Experimental.

Condensation of Thiocarbohydrazide with Substituted Phenanthraquinones and their Monoximes.

Di-(2-bromophenanthraquinone)-thiocarbohydrazone.—2-Bromophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid for a few minutes ; the precipitated thiocarbohydrazone was washed with water and crystallised from pyridine in red needles, m. p. 286°. (Found: N, 8·82. $C_{29}H_{18}O_2N_4SBr_2$ requires N, 8·69 per cent.).

2-*Thioketo*-bis-(5-*bromophenanthro*-1 : 2 : 3-*triazole*).—2-Bromophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution for about half an hour. The triazole separated on long standing ; this was collected and crystallised from acetic acid in red microscopic needles, m. p. 145°. (Found : N, 13·24. $C_{30}H_{14}N_6SBr_2$ requires N, 13·16 per cent.).

Di-(2:7-*dibromophenanthraquinone*)-*thiocarbohydrazone*.—2 : 7-Dibromophenanthraquinone and the hydrazide hydrochloride in acetic acid solution yielded at once the thiocarbohydrazone. This was crystallised from pyridine in brown-red needles, m. p. 260°. (Found : N, 7·12. $C_{30}H_{14}O_2N_4SBr_4$ requires N, 6·98 per cent.).

2-*Thioketo*-bis-(5 :10-*dibromophenanthro*-1 :2 : 3-*triazole*).—2 : 7-Dibromophenanthraquinonemonoxime and the hydrazide hydrochloride in acetic acid solution gave the triazole separating in orange crystals. Crystallised from acetic acid it forms orange needles, m. p. 210°. (Found : N, 10·70. $C_{30}H_{12}N_6SBr_4$ requires N, 10·55 per cent.).

Di-(2-*nitrophenanthraqninone*)-*thiocarbohydrazone*.—2-Nitrophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid solution. The hydrazone separated was crystallised from acetic acid in dull red needles, m. p. 220°. (Found : N, 14·62. $C_{30}H_{16}O_6N_6S$ requires N, 14·50 per cent.).

2-*Thioketo*-bis-(5-*nitrophenanthro*-1 :2 :3-*triazole*).—2-Nitrophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution for one hour. The solution on cooling was diluted with water when the triazole was precipitated as a dirty brown amorphous powder. It was crystallised from alcohol in brown microscopic rectangles, m. p. 200°. (Found : N, 19·57. $C_{30}H_{14}O_4N_8S$ requires N, 19·65 per cent.).

Di-(4-*nitrophenanthraquinone*)-*thiocarbohydrazone*.—4-Nitrophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid solution for two hours. The hydrazone was precipitated from solution with water and the precipitate crystallised from alcohol in vermillion red needles, m. p. 155°. (Found : N, 14·55. $C_{30}H_{16}O_6N_6S$ requires N, 14·50 per cent.).

Di-(4 :5-*dibromophenanthraquinone*)-*thiocarbohydrazone*.—4 : 5-Dibromophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid when the hydrazone separated in orange red crystals. This was crystallised from pyridine in rectangles of the same colour. It turns black at 260° and melts at 270°. (Found : N, 7·19. $C_{30}H_{14}N_4SO_2Br_4$ requires N, 6·98 per cent.).

2-*Thioketo*-bis-(7:8-*dibromophenanthro*-1:2:3-*triazole*).—4:5-Dibromophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid. The precipitated triazole was purified by crystallisation from pyridine in red rectangles, m. p. 235°. (Found: N, 10·68. $C_{29}H_{13}N_6SBr_4$ requires N, 10·55 per cent.).

Di-(4:5-*dinitrophenanthraquinone*)-*thiocarbohydrazone*.—4:5-Dinitrophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid solution for one to two hours. The hydrazone precipitated with water was crystallised from alcohol in red microscopic rectangles, m. p. 162°. (Found: N, 16·92. $C_{29}H_{14}O_{10}N_8S$ requires N, 16·81 per cent.).

2-*Thioketo*-bis-(7:8-*dinitrophenanthro*-1:2:3-*triazole*).—4:5-Dinitrophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution for one hour. The solution was diluted with water and the precipitate crystallised from alcohol in brown rectangles, m. p. 160°. (Found: N, 21·34. $C_{14}H_{12}O_8N_{10}S$ requires N, 21·21 per cent.).

Di-(2:7-*dinitrophenanthraquinone*)-*thiocarbohydrazone*.—2:7-Dinitrophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid for a quarter of an hour and the triazole precipitated with water was crystallised from alcohol in rectangles of dark colour, m. p. above 300°. (Found: N, 16·62. $C_{29}H_{14}O_{10}N_8S$ requires N, 16·81 per cent.)

2-*Thioketo*-bis-(5:10-*dinitrophenanthro*-1:2:3-*triazole*).—2:7-Dinitrophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution for an hour and the precipitated triazole was crystallised from dilute acetic acid in red needles which turn black at 250° and do not melt at 295°. (Found: N, 21·26. $C_{29}H_{12}O_8N_{10}S$ requires N, 21·21 per cent.).

Carbohydrazide and the Derivatives of Phenanthraquinone and their Monoximes.

Diphenanthraquinone-carbohydrazone.—Phenanthraquinone and carbohydrazide hydrochloride were heated in acetic acid solution when the hydrazone separated immediately. This was collected and crystallised from pyridine in orange yellow needles, m. p. 285°. (Found: N, 11·86. $C_{29}H_{18}O_2N_4$ requires N, 11·81 per cent.).

2-*Keto*-bis-(*phenanthro*-1:2:3-*triazole*).—Phenanthraquinone monoxime and the hydrazide hydrochloride were heated in acetic

acid solution for two hours. The separated triazole was crystallised from pyridine in bright yellow rectangles, m.p. 272°. (Found: N, 18·21. $C_{28}H_{16}ON_6$ requires N, 18·10 per cent.).

Di-(2-*bromophenanthraquinone*)-*carbohydrazone*.—2-Bromophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid solution for half an hour. The solution was diluted with water and the precipitated triazole was crystallised from alcohol in brown rectangles, m. p. 275°. (Found: N, 9·03. $C_{28}H_{16}O_2N_4Br_2$ requires N, 8·92 per cent.).

2-*Keto*-bis-(5-*bromophenanthro*-1:2:3-*triazole*).—2-Bromophenanthraquinonemonoxime and the hydrazide hydrochloride in acetic acid solution were heated for twenty minutes. The precipitated triazole that separated (a further quantity being obtained on cooling) was crystallised from acetic acid in brown needles, m. p. 245°. (Found: N, 13·64. $C_{28}H_{14}ON_6Br_2$ requires N, 13·51 per cent.).

Di-(2-*nitrophenanthraquinone*)-*carbohydrazone*.—2-Nitrophenanthraquinone and the hydrazide hydrochloride in acetic acid solution were heated only for a few minutes when the hydrazone separated. This was collected and crystallised from nitrobenzene in brown rectangles, m. p. 280°. (Found: N, 15·14. $C_{28}H_{16}O_7N_6$ requires N, 15·00 per cent.).

2-*Keto*-bis-5-*nitrophenanthro*-1: 2: 3-*triazole*).—2-Nitrophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution, the triazole beginning to separate almost immediately. After ten minutes the solution was filtered and the residue was crystallised from acetic acid in greenish yellow needles, m. p. 192°. (Found: N, 20·30. $C_{28}H_{14}O_6N_8$ requires N, 20·22 per cent.).

Di-(4-*nitrophenanthraquinone*)-*carbohydrazone*.—4-Nitrophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid solution. After five minutes the separated crystals were filtered and crystallised from pyridine in yellow needles, which turn red at 190° and melt at 240°. (Found: N, 15·12. $C_{28}H_{16}O_7N_6$ requires N, 15·00 per cent.).

2-*Keto*-bis-(7-*nitrophenanthro*-1: 2: 3-*triazole*).—4-Nitrophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution for forty-five minutes. The triazole separated in greenish yellow needles, m. p. 200°, which were found to be insoluble in all solvents. (Found: N, 20·33. $C_{28}H_{14}O_8N_8$ requires N, 20·22 per cent.).

Di-(2:7-*dibromophenanthraquinone*)-*carbohydrazone*.—2:7-Dibromophenanthrquinone and the hydrazide hydrochloride were heated in acetic acid solution for twenty minutes, the hydrazone separating in orange red needles. These were crystallised from nitrobenzene. It turns red at 280° and melts at 295°. (Found: N, 7·34. $C_{29}H_{14}O_2N_4Br_4$ requires N, 7·12 per cent.).

2-*Keto*-bis-(5:10-*dibromophenanthro*-1:2:3-*triazole*).—2:7-Dibromophenanthraquinonemonoxime and the hydrazide hydrochloride in acetic acid solution were heated for half an hour. The solution was diluted with water and the pricipitated triazole was crystallised from alcohol in orange rectangles, m. p. 210°. (Found: N, 10·89. $C_{29}H_{13}ON_6Br_4$ requires N, 10·76 per cent.).

Di-(2:7-*dinitrophenanthraquinone*)-*carbohydrazone*.—2:7-Dinitrophenanthraqninone and the hydrazide hydrochloride were heated in acetic acid solution when the hydrazone separated in dirty yellow crystals. This was recrystallised from nitrobenzene in yellow microscopic rectangles, m. p. above 300°. (Found: N, 17·43. $C_{29}H_{14}O_{11}N_8$ requires N, 17·23 per cent.).

2-*Keto*-bis-(5:10-*dinitrophenanthro*-1:2:3-*triazole*).—2:7-Dinitrophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution for fifteen minutes. The solution on cooling was filtered from the solid residue which was crystallised from acetic acid in greenish yellow needles, m. p. 230°. (Found: N, 21·87. $C_{29}H_{13}O_9N_{10}$ requires N, 21·74 per cent.).

Di-(2: 5-*dinitrophenanthraquinone*)-*carbohydrazone*.—4:5-Dinitrophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid solution. The hydrazone was crystallised from nitrobenzene in yellow rectangles, m. p. 295°. (Found: N, 17·82. $C_{29}H_{14}O_{11}N_8$ requires N, 17·23 per cent.).

2-*Keto*-bis-(7: 8-*dinitrophenanthro*-1:2:3-*triazole*).—4:5-Dinitrophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid for twenty minutes. After cooling the solution was diluted with water and the precipitated triazole was crystallised from dilute acetic acid in yellow needles, m. p. 160°. (Found: N, 21·65. $C_{29}H_{13}O_9N_{10}$ requires N, 21·74 per cent.).

Di-(4:5-*dibromophenanthraquinone*)-*carbohydrazone*.—4:5-Dibromophenanthraquinone and the hydrazide hydrochloride were heated in acetic acid. The hydrazone was crystallised from pyridine in reddish yellow rectangles, m. p. above 300°. (Found: N, 7·25. $C_{29}H_{14}O_2N_4Br_4$ requires N, 7·12 per cent.).

2-*Keto*-bis-(7 : 2-*dibromophenanthro*-1 : 2 : 3-*triazole*).—4 : 5-Dibromophenanthraquinonemonoxime and the hydrazide hydrochloride were heated in acetic acid solution for ten minutes and the separated triazole was crystallised from pyridine in yellow rectangles, m. p. 273°. (Found: N, 10·82. $C_{29}H_{13}ON_6Br_4$ requires N, 10·76 per cent.).

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Chemical Reactions under Electrodeless Discharge.

By

S. S. Bhatnagar, Rama Krishna Sharma and N. G. Mitra.

McVicker, Marsh and Stewart (*J. Chem. Soc.*, 1923, **123**, 642, 817, 2147 and subsequent papers) have studied the Tesla-luminiscence spectra of several organic substances and explained the importance of band and line spectra in bringing out the configuration of molecules in them. Recently, Bhatnagar, Shrivastava, Mathur and Sharma employed the electrodeless Tesla discharge in order to investigate the Tesla-luminiscence spectra of bromine, iodine and some organic substances and some of their results have already been communicated to the *Philosophical Magazine*.

While examining the Tesla-luminiscence spectra of organic substances, it was noticed by Bhatnagar and his colleagues that there existed a close similarity in the spectra of phenanthrene and anthracene, also of menthol and camphor. This led them to suspect that some sort of a chemical transformation might be going on in the discharge tube and this similarity observed might be due to the common part of the molecule obtained as a result of the decomposition of the substances examined. Further it was noticed that when at the end of the experiment the tube was taken out for cleaning, the product left behind was quite different in colour from the one originally taken. Evidently it seemed to have undergone some chemical change due to the electrodeless discharge. Reference to this has already been made in the Presidential Address of the Chemistry Section in the Fifteenth Session of the Indian Science Congress held at Calcutta in January, 1928, by one of us (S_1 S_2 B_3).

In the present investigation an account has been presented of the attempts made to identify the compound obtained from naphthalene.

It will be of interest to recall some of the previous work on the subject. McVicker, Marsh and Stewart (*loc. cit.*) examined a large number of organic substances including naphthalene but they did not find in any case a chemical change taking place. They noticed, however, while examining the Tesla-luminiscence spectra of benzene, that particles of carbon got deposited in the Tesla tube and that the benzene was charred. These workers, however, did not employ the

electrodeless discharge and heated the substance in order to vaporize them.

While the present investigation was in progress there appeared in an issue of the *Chemistry and Industry* (March 23, 1928) the report of the Thirteenth Annual Guthrie Lecture of the Physical Society, London, delivered by Sir J. J. Thomson. In his lecture he introduced to the notice of the audience—

(*a*) a new photo-electric effect,
(*b*) a method of obtaining the "Heaviside layer",
(*c*) a new method of synthesis.

Regarding (*c*) he found "that ordinary magnesium oxide combined with oxygen in the discharge tube to form a new oxide. Enquiry amongst his chemical friends had failed to elicit any information as to the known existence of this new oxide but he was informed by a chemical manufacturer that he manufactured a hundred-weight of it weekly. Calcium oxide and zinc oxide can be similarly oxidised in the discharge tube to form higher oxides. The rate of combination can be readily observed being metrical, and this new method was strongly recommended to the attention of the chemists as one offering every prospect of a means of effecting all sorts of combinations. Amongst all the substances he had tried, "helium" was the only one he had failed to oxidise.

Experimental.

The apparatus for obtaining the electrodeless discharge is the same as described in the paper communicated to the *Philosophical Magazine*. It consisted of a dental X-ray transformer, the primary of which was fed by an A. C. current. The secondary was connected to the primary of a Tesla coil, with a condenser and a spark gap in parallel to the Tesla. The secondary of the Tesla was connected to the ends of a solenoid covering the outer surface of the discharge tube, which consisted of a hard glass tube 25 cms. long. One end of it was finely ground where a quartz or glass plate could be cemented on or removed as desired. The other end was suitably narrowed to take a thick rubber tubing joint. Evacuation was done by means of a Cenco-Hyvac pump and between this and the discharge tube, a wash-bottle was included to catch the organic vapours.

The discharge tube was thoroughly cleaned and dried and a thin layer of the substance was spread on its inner surface, after which the quartz plate was cemented on. All the joints were sealed with

Everett's vacuum wax to prevent leakage. The substance chosen was an extra pure sample of Merck's naphthalene freshly resublimed. It was exposed to the action of the discharge for three hours in course of which the tube was occasionally shaken to expose fresh layers. Prolonged exposures carbonized the sample completely and a greater quantity of the substance at one instance did not help much to increase the yield. So the tube had to be exposed a number of times. The glow obtained ranged from bluish violet to yellowish white. When the exposure is finished it was always found that a portion of the substance got carbonized and the substance changed colour from white to yellowish brown. Most of it was removed by scrubbing while the portion that was carbonized could only be washed out by chloroform and stuck to the walls of the tube as a resinous matter.

The substance thus obtained was drained on a porous plate and left overnight to remove the gummy matter. It was then refluxed several times with chloroform till the solvent ceased to give any colour on boiling. The residue left behind was mostly charred naphthalene and was discarded. From the filtrate the solvent was got back by distillation and the concentrated chloroform extract evaporated off on a watch glass whereby a brown crust was obtained, which did not give a sharp melting point as it ranged between 70°-80°. This stuff consisted of unchanged naphthalene together with a new compound that is formed.

Separation of the Compound.—The brown mass, which was soluble in chloroform and in hot benzene, was separated from naphthalene either by refluxing with hot alcohol or by steam distillation in which case naphthalene got easily removed. The brownish black residue left after steam distillation was then boiled with alcohol in order to remove further quantities of naphthalene. The substance thus obtained on drying did not melt even at 300°.

Purification of the Substance.—It was further purified on refluxing with animal charcoal in chloroform solution to remove all the colouring and resinous matter present. The solution was then carefully filtered to revove the fine suspension of charcoal and the bulk was concentrated by distilling off the liquid. It was then dropped in excess of ether, when a heavy brown precipitate was obtained. This also did not melt even at 350°, but near about 300° the subs tance turned black, and shrinking of the mass took place.

Analysis of the Compound.—Qualitative analysis showed only the presence of carbon and hydrogen in the compound, which could be

detected by the usual tests for the elements. It burnt with a smoky flame and left no residue on the platinum foil when heated on it. Tests for the detection of groups failed to give any definite information. No addition product of any sort could be obtained. It was, however, completely soluble in chloroform and benzene, but very slightly in ether and alcohol and partly in acetone. Yield is very low, about 1 to 2 per cent. at the most on the above conditions.

Quantitative estimations were made of the elements present in the compound and the result of the combustion experiment was as follows:—

0·1050 gm. of the substance gave 0·3413 gm. of CO_2 and 0·0596 gm. of H_2O.

Therefore, Carbon=88·64, Hydrogen=6·30, Oxygen=5·06 per cent. (by difference).

The molecular weight of the compound was determined by the cryoscopic method and found to be 318.

The empirical formula calculated on the strength of the combustion experiment comes to $C_{24}H_{10}O$ and the molecular weight calculated according to this would be 324. The difference between the two values was, however, within the experimental errors. Hence the resulting compound obtained from naphthalene exposing the same to electrodeless discharge, has got the composition $C_{24}H_{10}O$. Further work on the determination of the constitution of the compound is in progress.

It has also been observed that the following substances decompose in the manner shown against them, when exposed to the Tesla discharge:

$PbSO_4$ changes to $PbSO_3$ and PbS
$CaSO_4$,, ,, $CaSO_3$
$KBrO_3$,, ,, KBrO and KBr
KIO_3 ,, ,, KI and I_2
$KClO_3$,, ,, KClO and KCl.
$PbSO_4 + Mg$ gives $PbS + MgO_2$.

Quantitative measurements will be communicated shortly.

We are thankful to Dr. S. Krishna for much valuable help during the course of this investigation.

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Catalytic Preparation of Alkyl-anilines. Part I.

By Bankim Chandra Roy.

Methyl and ethyl anilines (both mono- and di-) are extensively used in the manufacture of dyestuffs. The usual method of their preparation consists in heating aniline with the corresponding alcohol and sulphuric acid in an autoclave at a pressure of 25-30 atmospheres to a temperature of 230-35°. This method has got two main drawbacks—

(1) That it is not a continuous method, and (2) that a very high pressure is necessary increasing thereby the cost of production. Besides, the autoclave is required to be lined with enamel in view of the acid employed.

Attempts have been made from time to time to find an easier method of preparation by the use of suitable catalysts. Mention may be made of two important works in this direction.

(1) A German patent by Knoll & Co. claims that an almost quantitative yield may be obtained by heating aniline with the corresponding alcohol in the presence of a small quantity of iodine as catalyst to a temperature of 230°. In this case also the process is not a continuous one, and high pressure has to be maintained in order to raise the temperature to 230°. No mention, however is made in the original paper about the pressure required.

(2) Mailhe and de Godon claim that by using alumina as catalyst, a mixture of mono- and di-alkyl anilines is obtained by using a temperature of about 430°. They pass the mixed vapour of aniline and the alcohol over the catalyst kept at the temperature mentioned above. By passing the mixture a second time over the catalyst, practically the whole is converted into dimethyl or diethyl aniline.

The present work is an attempt to prepare the bases by using thoria as a catalyst. Mailhe and de Godon worked with this catalyst before but gave it up, the yield obtained by them was found to be very poor. The experiment was repeated and the

catalyst was prepared by starting with thorium nitrate and precipitating the oxalate. On burning the oxalate, the oxide was obtained in a very fine state of division. Three experiments were carried out with this powdered thoria at different temperatures and it was found that the percentage of conversion was rather low:

Temperature.	Conversion.
370°–380°	29 per cent.
430°–440°	40
440°–450°	42

So even at the high temperature employed about 60% of the aniline remained unchanged.

A modification was made in the preparation of the catalyst by depositing thoria in asbestos in the hope that better results might be achieved in this way as a greater surface of the catalyst would be exposed to the mixed vapour of alcohol and aniline. For this purpose, asbestos was first purified by digesting with hydrochloric acid and washing thoroughly till free from acid. Then it was soaked with a solution of thorium nitrate, dried in the steam-oven and then finally strongly heated, when the nitrate decomposed with evolution of nitrous fumes and thoria was deposited in a fine state of division. The results obtained by using this was quite satisfactory as will be seen from the following—

25 C.c. aniline and 25 c.c. ethyl alcohol were taken in each experiment, the amount of alcohol corresponding to the formation of diethylaniline. The results were as follows:—

Temperature.	Conversion.
350°–360°	63·4 per cent.
370°–75°	66·6
,,	68·0
385°–390°	66·7

So even by using a lower temperature the yield is increased from 40 to 66 per cent.

The experiment was repeated with methyl alcohol, 25 c.c. of aniline and 25 c.c. of methyl alcohol being used. The result are as follows:—

Temperature.	Conversion.	Monomethyl aniline.	Dimethyl aniline.
410°–420°	72·8 %	32·8 %	40 %
,,	67	29·4	37·6
420°–430°	75	45	30·0

Here also we find that the yields are quite good.

The percentage of conversion was determined in the following way.

A standard solution of the sodium salt of 2-naphthol-3:6-disulphonic acid (R-salt) was prepared by titrating with a diazo solution of aniline. The dyestuff formed settles down and a filter paper is spotted with the clear solution and also with R-salt solution and the end point is reached when just a faint line appears at the junction of the two spots.

Solution of R-salt was made by dissolving 3·7010 gm. in 250 c.c. of water. Aniline (1·4262 g.) is added to concentrated hydrochloric acid (3 c.c.) and made up to 250 c.c. so that 1 c.c.=0·0057 gm. aniline. 20 C.c. of this aniline solution is taken, diazotised and made up to 100 c.c. (1 c.c. diazo solution=·00114 gm. aniline).

5 C.c. of R-salt were taken in a beaker, a few drops of Na_2CO_3 solution and some common salt added and cooled. It is then titrated with the diazo solution. Vol. of diazo solution required=9 c.c. Hence 5 c.c. R-salt=·00114×9=·01026 gm. aniline.

Now in estimating the amount of aniline contained in the products, a known weight of the sample is taken and diazotised, the amount of $NaNO_2$ added being sufficient to react with the whole of the sample if it consisted of aniline solely—and then made up to a known volume. A known vol. of R-salt was then titrated with this diazo solution and from the volume of the latter the percentage of aniline in the sample was calculated. The results obtained are as given above.

Estimation of Mono- and Di-derivatives in the Products.

This was carried out in the following way:—

A known weight of the sample (1—1·5 g.) was taken in a 100 c.c. flask and treated with 5 c.c. acetic anhydride at the ordinary temperature. After standing for ½ hour, 50 c.c. water is added and heated on the water-bath for about an hour to convert any acetic anhydride to acetic acid. By this means the acetyl derivatives of aniline and mono alkyl aniline are produced but the dimethyl aniline remains unaffected. After cooling, the liquid is diluted to a known volume and titrated with standard NaOH using phenolphthalin as indicator. A blank experiment is carried out at the same time using 5 c.c. acetic anhydride only and by difference the amount of acetic anhydride consumed in reacting with aniline and monomethyl aniline is ascertained. Multiplying the quantity of the acetic anhydride used up by $\frac{107}{51}$, we get the combined percentage of aniline and monomethyl aniline in terms of monomethylaniline (*a*). The percentage of aniline already found, is next converted into its equivalent of monomethyl aniline, multiplying by the factor $\frac{107}{93}$ (*b*). By subtracting (*b*) from (*a*) we get the percentage of monomethyl aniline. The percentage of dimethylan iline is finally obtained by difference.

Further experiments in this direction are in progress.

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The Role of Phosphates in the Oxidation of Glucose.

By A. N. Kappanna.

The oxidation of glucose is one of the most important chemical changes of the organism taking place at constant temperature and nearly constant alkalinity. An almost neutral phosphate mixture is known to be a constituent of many living organisms and this accounts for the maintenance of constant alkalinity. While constant alkalinity may be a determining factor, it is of importance to ascertain if phosphates by themselves exert any specific catalytic effect in the oxidation process. Lob (*Biochem. Zeit.*, 1911, **32**, 43 and subsequant papers), Witzemann (*J. Biol. Chem.*, 1920, **45**, 1) and Harden and Henley (*Biochem. J.*, 1921, **15**, 672) have studied the oxidation of glucose by hydrogen peroxide in the presence of phosphates. Witzemann found that disodium phosphate exerted a catalytic effect, for he found that even at constant alkalinity, the rate of oxidation was dependent upon the amount of disodium phosphates present in the reaction mixture. He was not able to say definitely whether any intermediate complex between the hexose and phosphate was responsible for the increased rate of oxidation ; but he found a parallelism to exist between the rate of decomposition of hydrogen peroxide in the phosphate mixtures and the rate of oxidation of glucose in the same phosphate mixtures. He suggested that a $Na_2HPO_4-H_2O$ complex might exist in solution and this might be the cause of the increased rate of oxidation. This observation, if correct, is of very great importance. The conclusion that can be drawn from Witzemann's results that phosphates do exert a catalytic effect in addition to playing the part of buffer mixtures is in partial agreement with the views of Lob, while Harden and Henley opine that the only part played by the phosphates is the regulation of alkalinity.

If both glucose and hydrogen peroxide form complexes in solution with phosphates, the problem of investigating the nature of such complexes becomes difficult in a mixture of these three substances. It occurred to the writer that some light may be thrown on the

problem, by studying firstly the rate of oxidation of glucose with an oxidising agent satisfying the following conditions: (1) It should not ordinarily react with glucose in acid or neutral solutions. (2) It should be able to oxidise glucose in alkaline solutions and in particular at small concentrations of OH ions as can be obtained by using phosphate buffer mixtures. (3) It should not be such as would form any kind of complex with phosphates. Iodine was found to satisfy all these conditions. A study of the kinetics of oxidation of glucose by such an oxidising agent in the presence of phosphate buffer mixturss should at once enable us to determine with a certain amount of definiteness whether or not a hexose-phosphate complex comes into existence and enhances the rate of oxidation. Secondly a revision of the rate of decomposition of hydrogen peroxide in phosphate mixtures was thought necessary to see if Witzemann's observation about the complex formation could be confirmed.

Experimental.

Oxidation of Glucose by Iodine.

As stated above, iodine does not react with glucose in neutral and acid solutions, even on heating for several hours. It was therefore thought necessary first of all to determine the amount of iodine necessary to oxidise one molecule of glucose. A few initial experiments showed that the reaction takes place with measurable speed in phosphate buffer mixtures. Experiments carried on in buffer mixtures having p_H values between 7 and 8 showed that in all cases one molecule of iodine was taken up by one molecule of glucose, showing thereby that the oxidation progresses only to the stage of gluconic acid, just as in the case of oxidation with bromine (Bunzel and Mathews, *J. Amer. Chem. Soc.*, 1909, **31**, 464).

All the experiments described in what follows were carried out at a constant temperature (22°). The sample of glucose used was Merck's extra pure anhydrous powder. Care was taken to purify the disodium and monosodium phosphates by recrystallisation. The reaction was followed by titrating a known amount of the reaction mixture with standard sodium thiosulphate solution.

Initial experiments on velocity measurements showed that the reaction does not proceed smoothly like one of the second order. Figures given in Table I indicate that the velocity constant falls very rapidly as the reaction proceeds.

TABLE I.

20 c. c. of Na HPO_4 (0·33M)
5 c. c. of NaH_2PO_4 (0·33M) in 100 c. c. of reaction mixture.

Time in min.	Conc. of I_2 in mols. per litre.	Conc. of glucose in mols. per litre.	Bimol. K
0	0·0178	0·0817	—
10	0·0165	0·0804	9·361
20	0·0154	0·0793	8·993
40	0·0137	0·0776	8·221
100	0·0111	0·0750	5·685
200	0·00885	0·0728	4·554

Calculations showed that the data could not be made to fit into equations for reactions of higher orders. The fall in velocity constant should therefore be attributed to other causes. As the reaction progresses hydriodic acid and gluconic acids are formed and tend to reduce the alkalinity of the system. If the reaction is very sensitive to changes of p_H the fall in p_H may be one of the causes for the fall in velocity constant. Another factor tending to affect the velocity in the same direction is the formation and accumulation of iodide ions in the system ; these remove a portion of the active iodine as I_3. This latter cause could be detected and remedied by starting with a pretty large initial concentration of an iodide in the reaction mixture thereby maintaining the concentrations of I ions practically constant throughout the reaction. Experiments were next made to see if the reaction proceeds in conformity with unimolecular law when the initial concentration of glucose was made very large compared to the concentration of iodine, the concentration of the iodide ions being maintained constant as suggested above. The figures in Table II indicate that even with this modification the unimolecular velocity constant gradually falls as the reaction proceeds.

TABLE II.

4·5 gms. glucose ; 4·15 gms. KI ;

20 c. c. of 0·33M Na_2HPO_4
5 c. c. of 0·33M NaH_2PO_4 made up to 100 c. c.

25 c. c. of iodine soln. (0·149*N* in 0·25*N* KI).

Time in min.	$Na_2S_2O_3$	K/2·3
0	21·65 c. c.	
10	20·90	0·00154
30	19·40	0·00151
60	17·60	0·00150
90	16·40	0·01330
120	15·40	0·001233
180	13·65	0·001113
300	11·50	0·000916
∞	0	

These figures further lead to the inference that the fall in velocity constant is not so much due to the formation of I_3 ions but mainly due to some other more powerful factor. An experiment made under the same conditions but with double the quantity of glucose showed that the time for half change in regard to the disappearance of iodine was exactly half as in the above experiment. This shows that the reaction is really unimolecular with respect to iodine. The above experiments were carried out at constant alkalinity with a phosphate buffer mixture (p_H =7·41). If the reaction is really unimolecular with respect to iodine the only possible inference that could be drawn at this stage with regard to the fall in velocity constant appears to be that the reaction is extremely sensitive even to such small changes of p_H as can be brought about by the addition of very small quantities of acids to buffer mixtures. The validity of this inference should be tested by making velocity measurements at different degrees of alkalinity. Since the preparation of such buffer mixtures involves the use of disodium and monosodium phosphates

in varying proportions it was thought necessary at first to see if at the same p_H the velocity was in any way dependent on the concentration of either Na_2HPO_4 or NaH_2PO_4.

Influence of the Concentration of Na_2HPO_4.

Tables III-VI contain results of velocity measurements made with different concentrations of Na_2HPO_4 and NaH_2PO_4 at the same alkalinity. In all these experiments 100 c.c. of the reaction mixture contained 9 gms. of glucose, 4·15 gms. of KI, 25 c.c. of 0·15 N iodine soln. in 0·25 KI and different quantities of phosphates as mentioned in each table.

TABLE III.

40 C.c. 0·033 *M* Na_2HPO_4; 10 c.c. 0·33 *M* NaH_2PO_4

Time in min.	$Na_2S_2O_3$	K/2·3
0	21·6 c.c.	...
10	20·65	0·00280
20	19·20	0·00256
30	18·15	0·00252
60	15·80	0·00226
120	12·35	0·00203
∞	0	

TABLE IV.

20 C.c. 0·33 *M* Na_2HPO_4; 5 c.c. 0·33 *M* NaH_2PO_4

0	21·60	0·00291
10	20·20	0·00273
20	19·05	0·00257
40	17·05	0·00224
60	15·85	0·00185
120	12·95	
∞	0	

TABLE V.

15 C.c. 0·33 *M* Na_2HPO_4; 3·75 c.c. 0·33 *M* NaH_2PO_4

0	21·80	—
10	20·50	0·00267
20	19·55	0·00237
40	17·90	0·00220
60	16·65	0·00195
120	14·05	0·00159
180	12·30	0·00138
∞	0	

TABLE VI.

10 C.c. (0·33*M*) Na_2HPO_4; 2·5 c.c. (0·33 M) NaH_2PO_4

Time in min.	$Na_2S_2O_3$	K/2·3
0	21·80 c.c.	—
10	20·45	0·00278
20	19·45	0·00248
40	18·00	0·00210
60	16·95	0·00182
120	14·85	0·00139
∞	0	

It will be noticed that the velocity contants in all the above experiments in the first few minutes have almost the same value thereby indicating clearly that the amount of either of the phosphates has nothing to do with the rate of reaction so long as p_H remains the same. It is also to be seen that in mixtures having a greater amount of disodium phosphate the rate of fall of velocity constant is not so great as in mixtures having lesser amounts of disodium phosphate.

Experiments were now made to determine the variation of velocity with p_H. The concentrations of glucose, KI and iodine in all these experiments were kept the same as in the above experiments ; only the amounts of phosphates were varied so as to produce different degrees of alkalinity. In Table VII are given the rates of reaction as measured in the first ten minutes in different mixtures.

TABLE VII.

p_H	K/2·3	p_H	K/2·3
7·0	0·000	7·6	0·0051
7·1	0·0008	7·8	0·0066
7·2	0·00179	8·0	0·0075
7·4	0·0029	...	...

These figures indicate that the reaction is very sensitive towards variation in p_H. The fact that in a phosphate mixture of $p_H = 7$ the reaction does not proceed at all, just as in a solution containing no phosphates is clear proof that phosphates by their mere presence cannot accelerate the oxidation of glucose. It is now easy to explain why on looking at Tables III-VI we find that the rate of fall of velocity constant at the same p_H is greater in mixtures containing lesser amounts of $Na\ HPO_4$ than in those containing greater amounts of it as the change in p_H for an addition of the same amount of acid to a solution containing a lesser amount of Na_2HPO_4 is greater than in the case of a solution containing a greater amount of the phosphate. It would therefore appear that the main factor determining the velocity of reaction is p_H and not the concentration of phosphates. We may conclude that phosphates do not form complexes in solution which get more easily oxidised than the free glucose molecule.

Decomposition of Hydrogen Peroxide in Phosphate Mixtures.

The decomposition of Merck's perhydrol in phosphate mixtures has been studied in the following experiments. In pure aqueous solutions this specimen of hydrogen peroxide was found to decompose at a slow but measurable rate at 60°, and the other velocity measurements were also made at this temperature. To 100 c.c. of either pure water or the phosphate buffer mixture 1 c.c. of Merck's perhydrol (18*N*) was added, 10 c.c. of the mixture pipetted out at different intervals, mixed with excess of dilute sulphuric acid and titrated against decinormal permanganate solution. In all

cases a small period of induction was observed before H_2O_2 began to decompose normally. This is in accordance with the observations of previous workers (Rice and Reiff, *J. Phys. Chem.*, 1927, **31**, 1353). Tables VIII and IX give data obtained in phosphate mixtures of p_H =7·6 and p_H =7·8 respectively.

TABLE VIII.

p_H = 7·6

Time in min.	$KMnO_4$	K (unimolecular)
0	18·00 c.c.	—
10	16·30 initial	—
20	13·60	0·00787
30	11·40	0·00776
40	9·55	0·00774
50	8·00	0·00774
60	6·85	0·00753
∞	0	

TABLE IX.

p_H = 7·8

0	17·85	—
10	15·40 initial	—
20	12·25	0·00994
30	9·80	0·00981
40	7·80	0·00985
50	6·25	0·00980
60	5·20	0·00943
70	4·30	0·00923
∞	0	Mean 0·00968

Table X contains results obtained in a series of experiments carried out at constant alkalinity but with different amounts of phosphates.

TABLE X.

C.c. of phosphates in 100 c.c. of mixture.

0·33 *M* Na_2HPO_4	NaH_2PO_4	K
5 c.c.	1·25 c.c.	0·006728
10	2·5	0·006714
15	3·75	0·006745
20	5·0	0·006732
40	10·00	0·006690
	Mean	0·006730

It is obvious from the table that the amount of disodium or dihydrogen phosphate does not matter at the same p_H. Table XI gives the velocity constants obtained in solutions of different degrees of alkalinity.

TABLE XI.

p_H of phosphate mixtures.	K
7·0	0·00060
7·20	0·00407
7·40	0·00678
7·60	0·00773
7·80	0·00968
8·00	0·01200
Pure water	0·00056

It will be noticed that the rates of decomposition in pure water and phosphate mixtures of $p_H = 7$ are almost identical. The results in this table show that the rate of decomposition is simply proportional to p_H; we are therefore led to the conclusion that no phosphate-hydrogen peroxide complex could exist in solution.

Summary.

The kinetics of the reaction between glucose and iodine in phosphate buffer mixtures has been studied at 22°. At constant alkalinity the rate of oxidation has been found to be independent of the amounts of phosphates present in the mixture.

The rate of reaction has been found to increase with increase in p_H. In neutral solutions and in a phosphate buffer mixture of p_H =7·0 the reaction does not proceed at all. These results indicate that no hexose-phosphate complex is formed in solution. The only part played by phosphates is the regulation of constant alkalinity.

Velocity of decomposition of hydrogen peroxide in water and in phosphate buffer mixtures has been studied at 60°. The results obtained lead to the conclusion that no phosphate-hydrogen peroxide complex is formed in solution. The velocity of decomposition increases with increase in p_H ; at constant alkalinity the amounts of phosphates present have no influence on this velocity.

Further work on the problem will be reported in a later communication.

I wish to express my gratitude to Professor J. C. Ghosh, at whose suggestion this investigation was made, for his kind interest in this work.

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Studies in Ring Formation. Part II. The Constitution of Mono-phthalyl-benzidine.

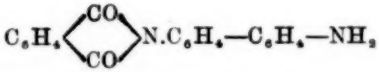
By Anukul Chandra Sircar and Prem Ranjan Sen-Gupta.

The present investigation is a continuation of the work of Sircar and De (this *Journal*, 1926, **3**, 245) and undertaken with the object of studying how far Kaufler's formula (*Annalen*, 1907, **351**, 151) for diphenyl and its derivatives could be supported.*

Gustav Koller (*Ber.*, 1904, **37**, 2880) condensed one molecule of benzidine with one molecule of phthalic anhydride and, from the insolubility of the resulting product in acids, concluded that both the amino groups in benzidine took part in the reaction. This view about the constitution of mono-phthalyl-benzidine was accepted and claimed by Kaufler (*loc. cit.*) as a strong proof in support of his theory.

It has now been found that, though insoluble in acids, Koller's mono-phthalyl-benzidine contains a free amino group. This has been proved by condensing the amino group with (1) various aldehydes, (2) another molecule of phthalic anhydride, (3) diazotising the amino group and coupling with β-naphthol.

These results establish the constitution of Koller's mono-phthalyl-benzidine to be



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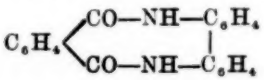
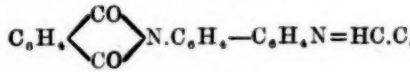


Experimental.

Benzylidene-phthalyl-benzidine,



* The experimental work described in this and the two following papers was finished in March, 1926, and the present authors had no chance of knowing anything about the work of Fevre and Turner (*J. Chem. Soc.*, 1926, 129, 2476) in the same line. The communication has been delayed due to certain unavoidable reasons.

To a solution of phthalyl-benzidine (1 g.) of Koller (*loc. cit.*) in 25 c.c. of hot nitrobenzene, benzaldehyde (0·5 g.) was added and the mixture boiled under reflux for half an hour. The crystals which separated on cooling were washed with alcohol and purified by recrystallisation from nitrobenzene. It forms rectangular, light-yellow plates, m.p. above 300°.

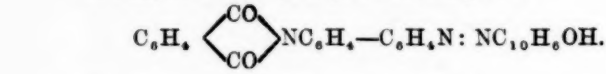
It is insoluble in alcohol, benzene, acetic acid or pyridine, but soluble in nitrobenzene. It is easily hydrolysed by acids or alkalis. This is evident from the smell of the aldehyde evolved on heating the substance for sometime with acids or alkalis. (Found : N, 7·50. $C_{27}H_{18}O_2N_2$ requires N, 6·96 per cent.).

Hydroxy-benzylidene-phthalyl-benzidine was prepared in the same way as the preceding compound from phthalyl-benzidine (1 g.) and salicylic aldehyde (0·6 g.) and obtained as yellow needles (from nitrobenzene), m.p. 297°. It resembles the previous compound in its properties. (Found : N, 6·85. $C_{27}H_{18}O_3N$, requires N, 6·7 per cent.).

Fevre and Turner (*loc. cit.* p. 2482) have also described this and the preceding compound, but the methods of preparation and purification are somewhat different.

m-*Nitrobenzylidene-phthalyl-benzidine*, prepared in the same way (boiling for 15 minutes) as the preceding compounds, from phthalyl benzidine (1 g.) and *m*-nitrobenzaldehyde (0·8 g.), separated from nitrobenzene in yellow needles, m.p. 280°. (Found : N, 9·52. $C_{27}H_{17}O_4N_3$ requires N, 9·39 per cent.).

Phthalyl-4-aminodiphenyl-4'-azo-β-naphthol,

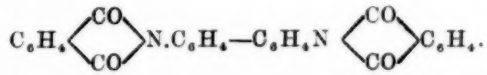


Phthalyl-benzidine (0·5 g.) was thoroughly triturated with 5 c.c of concentrated hydrochloric acid and then 20 c.c. of water added. The diazotisation was done in the usual way, the temperature of the reaction mixture being maintained at 20-22°. β-Naphthol (0·24 g.), dissolved in excess of caustic soda was then added to the diazotised solution. The resulting deep red, distinctly alkaline solution was left overnight. Next day the solution was acidified with hydrochloric acid when the azo-dye separated as a deep red precipitate. This was filtered, washed with water, dried and finally purified by successive crystallisations from alcohol, acetic acid and nitrobenzene. Microscopic crystals, m.p. 273-275°.

It is sparingly soluble in ether, more soluble in alcohol or acetic acid and easily soluble in pyridine or nitrobenzene. It dissolves in dilute caustic alkalis. (Found : N, 8·52. $C_{30}H_{18}O_3N_2$ requires N, 8·95 per cent.).

Fevre and Turner (*loc. cit.*) have also described, in a qualitative way, the formation of such an azo-dye.

Di-p-*diphthalyl-benzidine*,



This was obtained by boiling a solution of phthalyl-benzidine (0·5 g.) and phthalic anhydride (0·25 g.) in 25 c.c. of nitrobenzene for two hours and separated from hot nitrobenzene as yellow plates not melting below 300°. It is found to be identical with Bandrowski's diphthalyl benzidine (*Ber.*, 1884, **17**, 1181).

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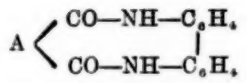
Studies in Ring Formation. Part III. The Condensation of Benzidine with Dibasic Acid Anhydrides.

By Anukul Chandra Sircar and Prem Ranjan Sen-Gupta.

In continuation of the preceding work the present paper deals with the constitution of the products obtained by the condensation of benzidine with dibasic acid anhydrides in general.

Naphthalic, camphoric, quinolinic, and diphenic anhydrides have now been condensed with benzidine and it has been found that wherever the reaction takes place between one molecule of the anhydride and one molecule of the diamine, only one amino group of the latter body takes part in the reaction—the other amino group remaining free. The presence of the free amino group is proved in each case by the fact that the reaction products can (*a*) condense with a molecule of an aldehyde and (*b*) be diazotised and coupled with a second component.

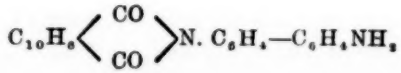
It is thus definitely established that in the reaction between one molecule of any dibasic acid anhydride and one molecule of benzidine a compound of the type—



as suggested by Koller (*Ber.*, 1904, **37**, 2880) and accepted by Kaufler (*Annalen*, 1907, **351**, 151) in the case of mono-phthalyl benzidine, is never formed.

Experimental.

Naphthalyl-benzidine,



Naphthalic anhydride (1 g.) and benzidine (1 g.) were finely powdered and thoroughly mixed in a mortar, 50 c.c. of water added and the mixture was heated in a suspended condition under reflux for about 15 minutes. Water was decanted off from the fused mass which solidified on cooling. It crystallised from hot pyridine in beautiful, yellow needles, m. p. above 300°.

It is insoluble in alcohol or benzene sparingly soluble in acetic acid but easily soluble in hot pyridine or nitrobenzene. It is insoluble in dilute acids or alkalis. It readily condenses with aldehydes and can be diazotised and coupled with phenolic bodies. (Found: N, 8·18. $C_{24}H_{16}O_2N_2$ requires N, 7·69 per cent.).

Dinaphthalyl-benzidine.—An intimate mixture of naphthalic anhydride (2 g.) and benzidine (0·9 g.) was heated in a test tube on the oil-bath at 250° for 3-4 hours. The resultant product crystallised from boiling pyridine in golden yellow needles, not melting below 300°.

It is insoluble in alcohol, benzene or acetic acid, but soluble in boiling pyridine or nitrobenzene. It does not dissolve in dilute acids or alkalis and does not condense with aldehydes. (Found: N, 5·18. $C_{36}H_{20}O_4N_2$ requires N, 5·14 per cent.).

Benzylidene-naphthalyl-benzidine,

$$C_{10}H_6 \begin{matrix} CO \\ CO \end{matrix} > N.\ C_6H_4—C_6H_4.\ N=HC.C_6H_5.$$

The crystals which separated on heating a mixture of naphthalyl-benzidine (0·5 g.) and benzaldehyde (1 c.c.) in pyridine (20 c.c.) for 10 minutes, were further purified by re-crystallisation from hot pyridine. It forms light-yellow, glistening plates melting at 297°.

It is insoluble in benzene, alcohol or acetic acid but soluble in pyridine or nitrobenzene. It is easily hydrolysed into its constituents. (Found: N, 6·55. $C_{31}H_{20}O_2N_2$ requires N, 6·19 per cent.).

Salicylidene-naphthalyl-benzidine was prepared from salicylic aldehyde (1 c.c.) and naphthalyl-benzidine (0·5 g.) in the same way and possesses properties similar to the preceding compound.

It forms rectangular, greenish-yellow plates melting at 283°, and does not dissolve in caustic alkalis. (Found: N, 5·95. $C_{31}H_{20}O_2N_2$ requires N, 6·00 per cent.).

m-*Nitro-benzylidene-naphthalyl-benzidine* was prepared from naphthalyl-benzidine (0·5 g.) and *m*-nitrobenzaldehyde (1 g.) in the same way as the preceding compound. It forms beautiful, yellow hexagonal prisms melting at 299°, and in its properties resembles the two previous compounds. (Found: N, 8·62. $C_{31}H_{19}O_4N_3$ requires N, 8·45 per cent.).

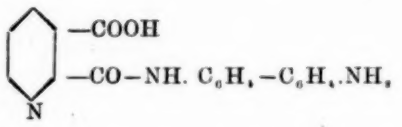
Camphoryl-benzidine.—A mixture of camphoric anhydride (1 g.) and benzidine (4·5 g.) was heated under suspension in 100 c.c. of water for 10 minutes. The contents were filtered hot and the residue freed from unreacted benzidine by boiling with water and filtering hot. It crystallises from dilute alcohol in fine colourless, clustering needles, m. p. 190°.

It is fairly soluble in alcohol, sparingly soluble in hot water, dilute acids or alkalis but insoluble in sodium carbonate solution. It easily condenses with aldehydes and can also be diazotised and coupled with phenols. (Found: N, 8·19. $C_{22}H_{24}O_2N_2$ requires N, 8·04 per cent.).

Quinolinyl-benzidine.—A mixture of quinolinic anhydride (0·73 g.) and benzidine (0·96 g.) suspended in 50 c.c. of benzene was heated under reflux for 10 minutes. The separated solid was treated with alcohol, to remove any unreacted material, and finally crystallised from nitrobenzene as light yellow, rectangular prisms, m. p. above 300°.

It is insoluble in alcohol, acetic acid, dilute acids or alkalis, but soluble in nitrobenzene. (Found: N, 13·51. $C_{19}H_{13}O_2N_3$ requires N, 13·33 per cent.).

The crude product before crystallisation readily dissolves in dilute alkali and sodium carbonate solutions. This is perhaps due to the fact that at first an additive compound, *viz.*, *p*-amino-diphenyl-quinolinamic acid—



is formed which in the process of crystallisation loses a molecule of water and is transformed into quinolinyl-benzidine.

p-*Amino-ditolyl-quinolinamic acid.*—A mixture of quinolinic anhydride (0·75 g.) and tolidine (1 g.) suspended in benzene (60 c.c.) was refluxed on a water-bath for 15 minutes. The separated solid was washed with benzene and finally crystallised from nitrobenzene in brilliant yellow needles, melting at 231°.

It is insoluble in alcohol, acetic acid or benzene but soluble in nitrobenzene. It dissolves in dilute alkali and sodium carbonate solutions. (Found: N, 11·63. $C_{21}H_{19}O_3N_3$ requires N, 11·63 per cent.)

N. B.—No quinolinyl-tolidine was obtained in this case (*cf.* the preceding experiment).

p-*Amino-diphenyl-diphenaminic acid.*—The solid which separated on refluxing for 15 minutes a mixture of diphenic anhydride (1·1 g.) and benzidine (0·9 g.) suspended in benzene (50 c.c.) was purified by crystallisation from dilute alcohol.

It forms microscopic crystals, m. p. 199°. It is insoluble in benzene or dilute acids, but soluble in alcohol, dilute alkali or sodium carbonate solutions. (Found: N, 6·35. $C_{26}H_{20}O_3N_2$ requires N, 6·86 per cent.).

The compound could not be made to lose a further molecule of water and form a ring, which would evidently be seven-membered.

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Thiophthalic Acids. Part I.

By Gopâl Chandra Chakravarti.

Various attempts have been made since 1874 to synthesise two important acids, *viz.*, mono- and di-thiophthalic acids. But up till now these endeavours have proved fruitless. In 1874 Schreder (*Ber.*, 1874, **7**, 704) treated phenyl phthalate in alcoholic solution with potassium hydrosulphide and appears to have obtained a very impure potassium thiophthalate from which hydrochloric acid set free the body $C_8H_4O_2S$. This body corresponds with thiophthalic anhydride and not with the acids. He represented the reaction by the following equations :—

$$C_6H_4(COOC_6H_5)_2+2KSH = C_6H_4(COSK)_2+2C_6H_5OH.$$

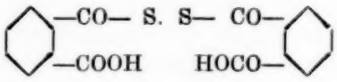
$$C_6H_4(COSK)_2+2HCl = C_6H_4\begin{matrix}CO\\ \diagup\diagdown\\ CO\end{matrix}S+H_2S+2KCl.$$

(I)

In 1884 Graebe and Zschokke (*Ber.*, 1884, **17**, 1175) found that thiophthalic anhydride and not the acid is obtained by acidification of the solution obtained by slowly adding phthalic chloride to a cold concentrated solution of sodium hydrogen sulphide. Later Reissert and Holle (*Ber.*, 1911, **44**, 3027) prepared a number of derivatives of both mono- and di-thiophthalic acids starting from thiophthalic anhydride but concluded like the previous investigators that these acids were somewhat stable in the form of their alkali salts in aqueous solutions, whereas the free acids were extremely unstable and therefore could not be obtained as such, the acids decomposing immediately into thiophthalic anhydride, m. p. 114°, and hydrogen sulphide.

Recently the author (Chakravarti and Saha, *J. Indian Chem. Soc.*, 1927, **4**, 141) made an attempt to condense phthalic anhydride with aromatic mercaptans in order to obtain dyes analogous to the phthaleins but found that the great reactivity of the mercaptanic hydrogen atoms led to the formation of thiophthalic esters instead

of the thiophthaleins. In that communication the authors expressed their intention of utilising the thiophthalates for the syntheses of mono- and di-thiophthalic acids. By carrying out the hydrolysis of ditolyl-dithiophthalate with alcoholic potassium hydrosulphide under various conditions, an acid containing sulphur and melting at 242° with decomposition was obtained. The acid however did not respond to the ordinary tests for 'thiol' group and the determination of its equivalent weight showed that it had a molecular weight almost double that required by monothiophthalic acid and was therefore dithio-dibenzoyl-*o* : *o'*- dicarboxylic acid (II).



(II)

The formation of this acid at once suggested that at an intermediate stage monothiophthalic acid must have been produced, and the latter might be obtained if the reaction could be properly moderated. But at a lower temperature the hydrolysis of the thioester would not take place. Hence a study of the interaction of potassium hydrosulphide and phthalyl chloride in alcoholic solution seemed desirable. It was found that the reaction proceeds very briskly even in the cold and from the products a number of compounds together with monothiophthalic acid have been isolated. A description of these products and their method of isolation are given in the experimental portion. From a study of the properties of monothiophthalic acid, the author generally agrees with the views expressed by previous investigators about the extreme unstability of the acid, but the hypothesis that it breaks down immediately on formation into thiophthalic anhydride should once for all be discarded. Because under ordinary conditions the anhydride was never obtained by the decomposition of the acid ; the product that was invariably obtained was the corresponding disulphide, dithiodibenzoyl dicarboxylic acid, evidently formed by the oxidation of the mercaptanic hydrogen atom. In fact the acid is so very reactive towards oxygen that it gets oxidised by the atmosphere even during processes of purification and crystallisation ; so that for a long time the disulphide was looked upon as the initial product of the reaction.

In the operations a sample of crystallised potassium hydrosulphide supplied by Kahlbaum was used. As this contains water of

crystallisation it is very difficult to indicate the exact mechanism of the reaction, which may have taken either of the courses:—

$$C_6H_4(COCl)_2 + 2KSH = C_6H_4(COSH)_2 + 2KCl.$$

$$C_6H_4(COSH)_2 + H_2O = C_6H_4\begin{cases}COSH\\COOH\end{cases} + H_2S \qquad (1)$$

or

$$C_6H_4(COCl)_2 + KSH + H_2O + KSH = C_6H_4\begin{cases}COSH\\COOH\end{cases} + 2KCl + H_2S \qquad (2)$$

Of the two alternatives, reaction (1) appears to be the more likely, because although the dithio acid has not been isolated in the pure state its existence has been confirmed from various facts. The extract obtained by aqueous carbonated alkalis from the ethereal solution of the reaction product on acidification gives a precipitate of the monothio acid or more generally its disulphide mixed with an acidic oil with very strong characteristic disagreeable odour. This oily acid gradually diminishes in quantity during purification and more and more of the solid acid is produced. This change therefore represents the second phase of reaction (1). Moreover, when the ethereal solution of the mixture of acids or their aqueous alkaline solution is kept exposed to the air for sometime a yellow precipitate insoluble in alkalis begins to appear which can only be formed by the elimination of hydrogen sulphide from dithiophthalic acid or of alkaline sulphides from its alkaline solutions:

In fact when such an alkaline solution is acidified after removal of the yellow precipitate, hydrogen sulphide is evolved plentifully and simultaneously thiophthalic anhydride also is formed in considerable quantity by the elimination of one molecule of hydrogen sulphide from a molecule of the acid. Thus dithiophthalic acid undergoes a threefold decomposition into monothiophthalic acid, thiophthalic anhydride and diphthalyl disulphide. The crude acid could not be purified from admixture with solvents and the monothio acid on account of its extreme instability and is under further investigation.

Experimental.

12 Gm. of potassium hydrosulphide are mixed with 125 c.c. of absolute alcohol and saturated with sulphuretted hydrogen in the cold and then gradually added to a cold solution of 15 gm. of phthalyl chloride in 75 c.c. of alcohol. A vigorous reaction at once begins. The reaction-bottle is well-corked, cooled by a freezing mixture to $-5°$ and allowed to stand for half an hour with occasional shaking. Then the vessel is removed to a shaking machine and the reaction is allowed to proceed there for about three hours at a temperature not exceeding 10°, and then the mixture allowed to stand overnight. The contents of the bottle are next poured on to about a litre of ice water and the aqueous mixture extracted with ether. The ethereal extract is washed thoroughly with cold water and then neutralised with a slight excess of a cold solution of sodium carbonate. A yellow precipitate (A) which is neither soluble in alkali nor in ether separates out at this stage and is removed. The ethereal extract (B) is kept for further treatment.

A part of the alkaline extract is neutralised with cold dilute hydrochloric acid and the precipitated stuff extracted with ether. This ethereal solution is dried over anhydrous magnesium sulphate and on slow evaporation deposits needle-shaped crystals, which are found to be difficultly soluble in ether. The product is therefore crystallised from a large quantity of absolute alcohol and obtained in the form of very light cream-coloured minute crystals, melting about 242° with decomposition. These are found to correspoud to dithio-dibenzoyl *o*:*o*′-dicarboxylic acid. (Found: C, 52·91; H, 2·84; S, 17·98. $C_{16}H_{10}O_6S_2$ requires C, 53·04; H, 2·76; S, 17·9 per cent.). The *potassium salt* is prepared by adding the calculated quantity of alcoholic caustic potash to an absolute alcoholic solution of the acid and evaporating part of the alcohol in vacuum. (Found: K, 18·01. $C_{16}H_8O_6S_2K_2$ requires K, 17·8 per cent.). The *lead salt* is obtained as a white crystalline precipitate by adding lead acetate solution to a solution of the potassium salt in water. The precipitate is washed with water, alcohol and ether. (Found: Pb, 36·15. $C_{16}H_8O_6S_2Pb$ requires Pb, 36·5 per cent.). The remaining portion of the alkaline extract was converted into the lead salt by means of lead acetate solution and the lead salt washed with water and alcohol and thoroughly dried. The powdered lead compound is suspended in anhydrous ether and decomposed by passing sulphuretted hydrogen.

The precipitate of lead sulphide is filtered off and the ethereal solution on concentration deposits almost colourless needle-shaped crystals of monothiophthalic acid which after recrystallisation from ether melts with decomposition at about 198°. (Found: C, 52·22; H, 3·8; S, 17·24. $C_8H_6O_3S$ requires C, 52·74; H, 3·28; S, 17·56 per cent.). Monothiophthalic acid is readily soluble in ether and alcohol. Its conversion into the less soluble disulphide is so rapid in presence of air that even during the evaporation of its ethereal solution it gets oxidised so that in the course of several preparations the disulphide dicarboxylic acid was the only compound obtained in the final stage. The ethereal mother-liquor, after removal of the monothio acid, leaves an oil with stongly acid character and characteristic disagreeable odour. From preliminary investigation this oil-acid is supposed to be dithiophthalic acid. Further investigation is in progress.

The *sodium salt* of monothiophthalic acid is obtained by adding the calculated quantity of aqueous sodium carbonate solution to an alcoholic solution of the acid. The filtered solution is concentrated to a small bulk, treated with absolute alcohol and again filtered. On keeping in contact with a small quantity of ether, the solution deposits colourless crystals of the sodium salt. (Found: Na, 20·10. $C_8H_4O_3SNa_2$ requires Na, 20·3 per cent.). The *lead salt* is obtained by adding an alcoholic lead acetate solution to an alcoholic solution of the acid. (Found: Pb, 53·21. $C_8H_4O_3SPb$ requires Pb, 53·48 per cent.).

The yellow precipitate (A) is washed with water, dried and repeatedly extracted with a large volume of alcohol. The alcohol removes a quantity of sulphur only. The deep yellow residue is dissolved in the minimum quantity of hot pyridine, which deposits on cooling a crop of very light needle-shaped egg yellow crystals which do not decompose on heating up to 320°. The compound is insoluble in ether, alcohol, benzene, etc., and in alkalis and is supposed to be diphthalyl disulphide. (Found: S, 19·26. $C_{16}H_8O_4S_2$ requires S, 19·51 per cent.).

The ethereal solution (B) is dehydrated with anhydrous magnesium sulphate and then slowly evaporated. Colourless needle-shaped crystals, m.p. 114°, are obtained. They are identical with thiophthalic anhydride. (Found: S, 19·42. $C_8H_4O_3S$ requires S, 19·51 per cent.). The ethereal mother-liquor, on complete evaporation, leaves an oil which is purified from admixed solid by distillation in steam.

The distillate is extracted with ether, dehydrated by anhydrous magnesium sulphate, filtered and the ether completely removed first on the water-bath and finally in a vacuum over sulphuric acid. The constitution of the oil has not been determined.

Hydrolysis of Ditolyl-dithiophthalate : Formation of Dithiodibenzoyl-o:o'-dicarboxylic Acid.—10 Gm. ditolyldithiophthalate and 7 gm. of potassium hydrosulphide are suspended in 75 c.c. of absolute alcohol and saturated with sulphuretted hydrogen. The mixture is heated in a sealed tube for 8—9 hours at 120°. The red solution is partially evaporated, treated with water and the aqueous solution decanted off from the insoluble oil, cooled by ice and treated with dilute hydrochloric acid. The precipitated mass is next treated with sodium carbonate solution and the solution washed with ether, filtered and reprecipitated with cold dilute hydrochloric acid. The solid is washed with water and crystallised from absolute alcohol. Cream-coloured needle-shaped crystals, m.p. 242° d. identical with those of dithiodibenzoyl-*o*:*o'*-dicarboxylic acid are obtained.

I desire to thank Sir P. C. Rây for his very kind interest and also Mr. R. K. Bhattacharyya, M.Sc., A.I.I.Sc. for rendering valuable help in the analytical work.

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The Mechanism of Photosensitisation and Photo-inhibition from the Point of View of Absorption Spectra.

By B. K. Mukerji and N. R. Dhar.

The phenomenon of photosensitisation has now been observed in numerous reactions by different investigators. Winther and co-workers (*Z. Wiss. Photochem.*, 1922, **21**, 168; 1913, **13**, 89), Sanyal and Dhar (*Z. anorg. Chem.*, 1923, **128**, 212) and others have shown that the decomposition of Fehling's solution, cupric ammonium-oxalate, Eder's mixture, a mixture of mercuric chloride and tartrate, etc., can be accelerated by ferric or uranyl salts under the influence of sunlight. A mixture of mercuric chloride and ammonium oxalate is almost insensitive to the light of a tungsten-filament lamp but it can be made sensitive to this light in presence of rosin.

Baur and co-workers (*Helv. Chim. Acta*, 1918, **1**, 186; 1924, **7**, 910; *Trans. Faraday Soc., October*, 1925, p. 629), Bhattacharya and Dhar (this *Journal*, 1927, **4**, 299), and others have shown that zinc oxide behaves as a very powerful sensitiser for numerous photo-chemical reactions.

Bäckström (*J. Amer. Chem. Soc.*, 1927, **49**, 1460), in a recent communication, observes that benzophenone and acetophenone act as sensitisers for the photochemical oxidation of benzaldehyde and heptaldehyde. Though a large number of sensitisers have come to light yet the mechanism involved in the process of sensitisation is not clearly understood.

Recently Baur and co-workers (*loc. cit.*) have introduced a theory according to which the main reacting constituent is supposed to be polarised in presence of the sensitisers. Some authors are of opinion that the sensitising substance combines with the reacting materials to form an intermediate compound. Sufficient experimental data are not however available for testing the correctness of either of these suggestions. Recently Ghosh and Mitra (this *Journal*, 1927, **4**, 353 ; 1928, **5**, 191) have measured the increased absorption of light consequent on the addition of uranyl and ferric salts to several organic acids.

The object of the present paper is to elucidate the mechanism of sensitisation and inhibition on the basis of spectral evidence. For this purpose the absorption spectra of the vario us constituents of a reacting system as well as of the sensitising or the inhibiting substance have been photographed. It is evident from these photographs that the amount of light absorbed by the reacting system changes markedly in presence of a sensitiser.

The following reactions have been investigated from the viewpoint of photo-sensitisation : —

(*i*) Reduction of Fehling's solution in presence of uranyl nitrate and ferric chloride.

(*ii*) Oxalic acid and chromic acid in presence of manganous sulphate and sulphuric acid.

(*iii*) Copper sulphate and potassium oxalate in presence of uranyl nitrate and ferric chloride.

The following reactions have been studied from the point of view of inhibition : —

(*i*) Formic acid and chromic acid in presence of manganous sulphate.

(*ii*) Oxidation of benzaldehyde in presence of hydroquinone.

(*iii*) Oxidation of benzaldehyde in presence of phenol.

The photographs were obtained with an Adam-Hilger Quartz Spectrograph (E 1 type) and Ilford Panchromatic plates were used throughout. An automatic copper arc (220 volts, 4·5 amp.) was used as the source of light. The absorbing substances were placed in rectangular neutral-tinted glass vessels having optically plane parallel ends.

As all the changes studied in this paper take place in ordinary sunlight it is desirable to restrict for the present the limits of the absorption spectra to the visible region of the spectrum. The spectrograph was set for the " first region " of the spectrum, that is, the region where photographs are obtainable within the limits λ 8000-3000Å. The emission spectrum of copper was taken as the comparison spectrum. Though panchromatic plates were used yet no sharp lines beyond λ 6162Å could be obtained towards the infrared region. Between λ 5700-5200Å no prominent line of copper is noticeable.

The following photographs have been obtained : —

Plate I (from top downwards).

(*i*) $UO_2(NO_3)_2$—N/20 and Fehling's solution.
(*ii*) $UO_2(NO_3)_2$—N/20.
(*iii*) $FeCl_3$—N/20 and Fehling's solution.
(*iv*) $FeCl_3$—N/20.
(*v*) Fehling's solution.

Plate II.

(*i*) $MnSO_4$—N/280, $(COOH)_2$—N/200 and chromic acid—N/440.
(*ii*) Oxalic acid—N/200.
(*iii*) Chromic acid—N/440.
(*iv*) Manganous sulphate—N/280.

Plate III.

(*i*) $FeCl_3$—N/25 and potassium oxalate—2N.
(*ii*) $CuSO_4$—N/35, $K_2C_2O_4$—2N and $FeCl_3$—N/25.
(*iii*) $UO_2(NO_3)_2$—N/25.
(*iv*) $CuSO_4$—N/35, $K_2C_2O_4$—2N and $UO_2(NO_3)_2$—N/25.
(*v*) Potassium oxalate—2N.
(*vi*) Copper sulphate—N/35.
(*vii*) $CuSO_4$—N/35 and $K_2C_2O_4$—2N.
(*viii*) Copper arc.

Plate IV.

(*i*) Chromic acid—N/350, formic acid—N/150 and $MnSO_4$—N/400.
(*ii*) HCOOH—N/150.
(*iii*) Manganous sulphate—N/400.
(*iv*) Chromic acid—N/350.
(*v*) Copper arc.

Plate V.

(*i*) Copper arc.
(*ii*) Hydroquinone in ethyl alcohol and benzaldehyde.
(*iii*) Benzaldehyde in ethyl alcohol.
(*iv*) Hydroquinone in ethyl alcohol.

Plate VI.

(*i*) Copper arc.
(*ii*) Phenol and benzaldehyde (both dissolved in ethyl alcohol).
(*iii*) Benzaldehyde in alcohol.
(*iv*) Phenol in alcohol.

It may be noted from the accompanying photographs that in the cases of photo-sensitisation there is always an increase in the absorption of light in presence of the photosensitiser. In fact the absorption spectra of the reacting mixtures in presence of the photo-sensitisers are almost identical with the spectra of the sensitisers themselves.

We have shown in a previous paper (Dhar, *J. Chem. Soc.*, 1917, **111**, 707) that though manganous sulphate acts as an accelerator in the case of the oxidation of oxalic acid by chromic acid yet it acts as a retarder in the reaction between formic acid and chromic acid. Similarly, phenol and hydroquinone act as inhibitors in the oxidation of benzaldehyde.

It will be seen from these photographs that in the case of photo-inhibitors, the absorption spectra of the reacting mixtures remain the same as that of the chief photoactive constituent. As regards the absorption spectrum of the mixture, formic acid and chromic acid in presence of $MnSO_4$, it may be pointed out that the spectral lines are identical with those obtained for chromic acid. In the cases of the oxidation of benzaldehyde in presence of hydroquinone and phenol it is evident that the absorption spectra of the mixtures, benzaldehyde-hydroquinone and benzaldehyde-phenol are similar to the absorption spectra of benzaldehyde which shows marked absorption in the visible region.

From the photographs it is evident that acceleration in light is always accompanied by an increased absorption of light.

The addition of uranium or iron salts to numerous mixtures reacting photochemically causes an increase in the absorption of light by the entire reacting system. Hence both uranium and iron salts act generally as photosensitisers. This increased absorption of light consequent on the addition of iron and uranyl salts has been reported as "exaltation" of the original reacting materials by Ghosh and Mitra (*loc. cit.*) in the cases of certain organic acids.

In the case of photo-inhibitors no such increase in absorption is noted. The spectra of the reacting substances remain practically unaffected by the presence of the non-reactive constituents.

We are trying to prove that substances which are chemically reactive show more marked absorption than substances which are not reactive. An alcoholic solution of benzaldehyde takes up

oxygen more readily than a solution of acetaldehyde, and the benzaldehyde solution shows more absorption than an acetaldehyde solution. Moreover, we have shown that the velocity of the reaction between ethyl alcohol and bromine is greater than that between methyl alcohol and bromine. According to Spring (*Bull. Accad. Belg.*, 1896, **31**, 246) ethyl alcohol shows more absorption than methyl alcohol. Hence we believe that chemical reactivity and capacity for absorption of radiations go hand in hand and the results are in support of the radiation hypothesis of chemical change.

Further work in this line is in progress in these laboratories.

Summary.

(1) Absorption spectra have been photographed using a quartz spectrograph of high dispersion of several mixtures containing uranyl nitrate and ferric chloride as photo-catalysts. The photographs show that in presence of uranium and iron salts there is marked increase of absorption of light and these two substances are well known for their photosensitising power.

(2) The addition of manganous sulphate to a mixture of oxalic acid and chromic acid markedly increases the absorption of light by the mixture, and we have proved that manganous sulphate is a marked positive catalyst for the above reaction.

Manganous sulphate acts as a negative catalyst in the reaction between formic acid and chromic acid and it does not cause an increase of the absorption of light when added to the mixture.

(3) Hydroquinone and phenol when added to benzaldehyde retards the oxidation of benzaldehyde and do not increase the absorption of light.

(4) It appears that photosensitivity and increase of absorption of light are closely associated.

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THE UNIVERSITY, ALLAHABAD.

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Plate I.

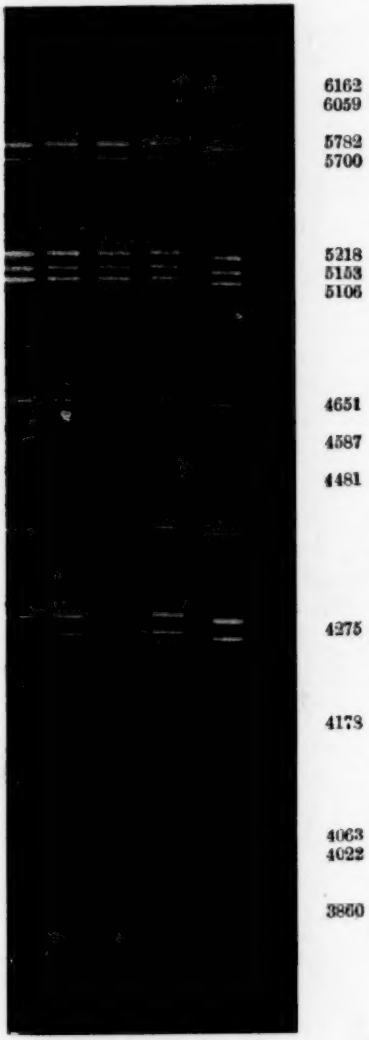
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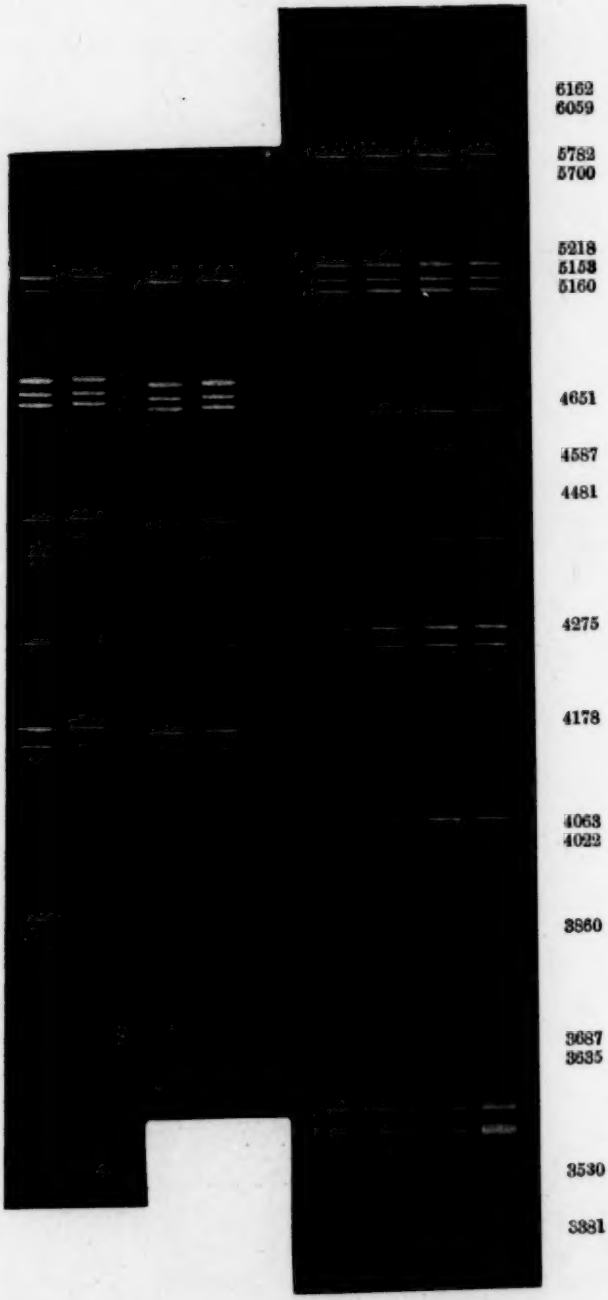
Plate III.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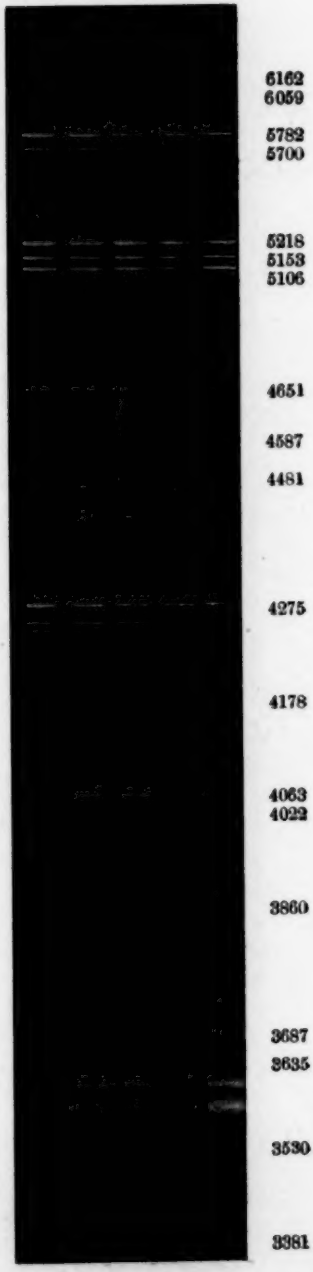
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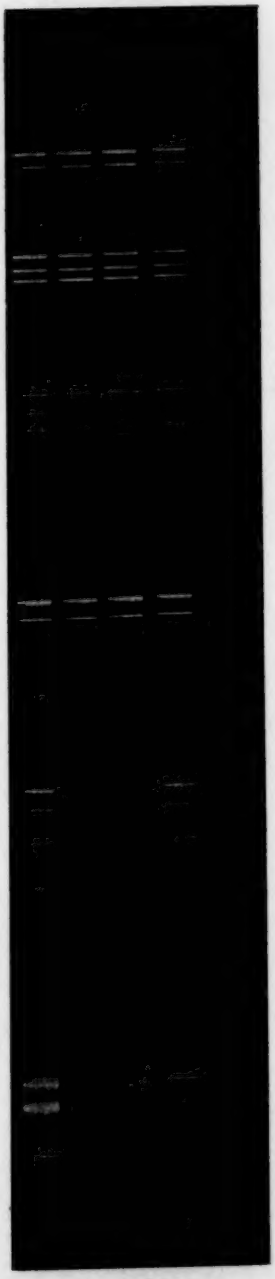
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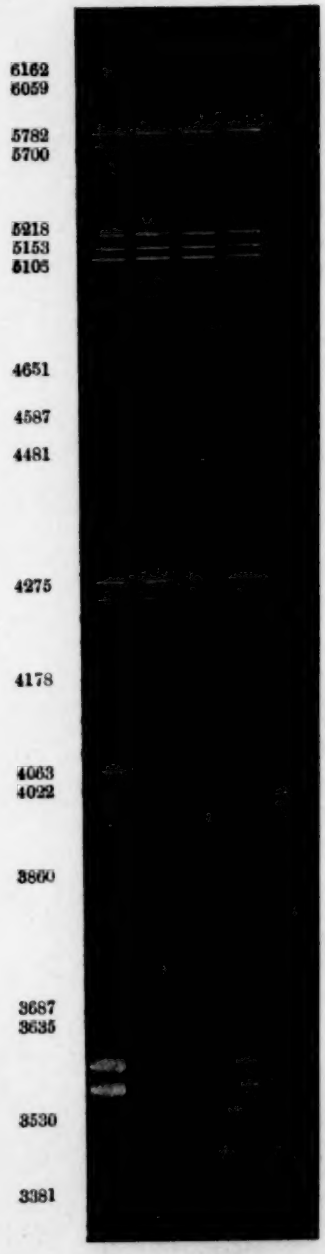
Plate VI.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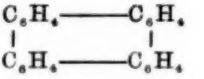
A Note on an Attempt to prepare *p*-Diphenylene.

By Anukul Chandra Sircar and Jnanendra Narayan Majumdar.

This note gives a further (compare Sircar and De, this *Journal*, 1926, **3**, 245) account of the works that have been done with the object of preparing *p*-diphenylene, which according to Kaufler's theory (*Annalen*, 1907, **351**, 151) must be the hypothetical parent hydrocarbon of which diphenyl and its substitution products are the derivatives.

As before (Sircar and De, *loc. cit.*) *p*: *p'*-di-iodo-diphenyl and finely divided copper powder (Natur Kupfer C) were used, and as the result of a large number of experiments carried out under varied conditions, it has now been found that if the reaction is carried out in a perfectly dry sealed tube at a temperature of 300-310°, a substance melting at 304-305° is obtained. From a determination of its molecular weight and study of other properties it appears to be tetraphenylene,



a hitherto unknown hydrocarbon. If the reaction is performed in a sealed tube, containing a small quantity of water, at 280-300°, the copper replaces the iodine atoms by hydrogen and diphenyl is formed.

It thus appears that, though *p*-diphenylene could not be prepared, as a result of the present investigation, (*a*) a new hydrocarbon has probably been obtained, and (*b*) under definite conditions, finely powdered copper can replace iodine atoms in an organic molecule by hydrogen.

Experimental.

Tetraphenylene.—An intimate mixture of *p*: *p'*-di-iodo-diphenyl (5 g.) and finely divided copper powder (10 g.) was heated in a dry sealed tube at 300-310° for 15 hours. The copper lost its lusture. The reaction product was extracted with boiling benzene from which, on concentration, the hydrocarbon separated as minute white plates, m. p. 304-305°.

It is insoluble in the cold in all the common organic solvents, but dissolves in hot nitrobenzene or pyridine and with difficulty in benzene. (Found: C, 94·89 ; H, 5·84. $C_{24}H_{16}$ requires C, 94·73 ; H, 5·26 per cent.). 0·3219 G. of the substance dissolved in 24·48 g. of pyridine gave elevation of boiling point 0·11° and 0·13°.

Found: M. W. =

(*i*) 350, 296 (Warner's method).

(*ii*) 343, 290 (Rose Innes' method).

(*iii*) 315, 266 (Walden's method).

$C_{24}H_{16}$ requires M. W. = 304.

Diphenyl.—An intimate mixture of 5 g. of *p*: *p*'-di-iodo-diphenyl with double the amount of copper powder and 1 c. c. of water was heated in a sealed tube at 280-300° for 5 to 6 hours, after which time the copper was found to have lost its lusture. The contents of the tube were extracted with ether, the ether distilled off, and the residue crystallised from alcohol in minute white plates (m. p. 70°). By determinations of the percentage composition, molecular weight and mixed melting point, and also by its conversion into *p*: *p*'-dibromo-diphenyl (prisms, m. p. 164°), the substance was dentified to be diphenyl.

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Received April 25, 1928.

Constitution of the Active Principle of *Chita*. Part I.

By Amaresh Chandra Roy and Sikhibhushan Dutt.

Chitraka or *Chita* as it is more commonly known in Bengal and the United Provinces is the root of a plant which grows throughout the year as cultivated or wild shrubs under three distinct botanical classifications: (1) *Plumbago rosea*, (2) *Plumbago zeylanica* and (3) *Plumbago europoea*. *P. rosea* is very common in Bengal whereas *P. zeylanica* is more generally met with in the U. P. *P.europoea* is comparatively rare in both the provinces principally because of the fact that being a comparatively more delicate plant it can only exist under cultivated conditions. *Chita* has been quite well known in our country from a very long time, and there are references to it in the classical works of Charaka, Susruta and Muhammad Husian. Therein its vesicant, stimulative, acrid and antiseptic properties are widely made use of in various prescriptions for dyspepsia, paralysis, rheumatism, cough, leprosy, plague and a host of other diseases. The caustic properties of Chita have also found illegal applications in causing abortions and poisoning, numerous cases of which have been recorded in the various works on Indian medical jurisprudence.

The active principle of Chita or 'plumbagin,' as has been named by the author, was first isolated by Dulong in 1885 (*Pharmacographica Indica*, Vol II, p. 332) by extracting the roots of *P.europoea* with ether and obtained in the form of shining yellow needles by crystallisation from alcohol. Later on Fluckiger in 1887 isolated the same substance in a slightly purer form from the roots of *P. zeylanica* by submitting them to steam distillation and extracting the distillate with ether. In 1888 Bettinck (*Haaxmans Tijdsch*, Jan., 1888) also isolated plumbagin from *P. rosea* in the form of yellow needles from hot water melting at 72°, and he was of the opinion that the composition of the substance was best represented by the formula $C_6H_{13}O_6$.

After these preliminary investigations dating back to more than forty years, there has not been any further publications about the constitution of Chita, and the following investigation was undertaken regarding the constitution of the substance which is decidedly of great physiological importance.

Plumbagin is present in all the three varieties of plants to a maximum of about 0·9-1 per cent. *P. rosea* and *P. zeylanica* contain approximately the same proportion of plumbagin whereas *P. europoea* contains much less. The exact proportion of plumbagin in these plants varies within wide limits according to the locality, growth, age, condition of the soil, season of the year and many other considerations. In general it is found that the bigger the plant and the drier the soil, the greater is the quantity of plumbagin found in the roots. It has also been found that fresh roots yield a much greater proportion of plumbagin than roots which have been stored for a considerable time. That is the reason why bazaar Chita yields comparatively so little of plumbagin. It is just possible that the plumbagin in the roots are destroyed to a considerable extent on long storage due to oxidation.

For extracting plumbagin the best solvent that has yet been found is petroleum ether (b. p. 70°-90°), and the substance is best crystallised from dilute alcohol. The melting point (78°) of plumbagin as isolated by the present authors is 6° higher than that obtained by Bettinck, which probably indicates a much purer specimen. The analytical data together with the molecular weight determined by the cryoscopic method in benzene point to the conclusion that plumbagin must be represented by the molecular formula $C_{11}H_{10}O_3$. On oxidation by neutral or alkaline potassium permanganate in the cold plumbagin yields benzoic and cinnamic acids, whereas by distillation with zinc dust it produces naphthalene and β-methyl-naphthalene. These facts together with the yellow colour and the penetrating quinone like smell of plumbagin make one liable to think that plumbagin might be a derivative of *p*-benzoquinone of α-naphthoquinone. This conclusion is also supported by the fact that plumbagin in acetic acid solution is very easily reduced by zinc dust to a colourless leuco compound, which is oxidised by atmospheric air back to yellow plumbagin with the greatest rapidity. Further confirmation of its quinone structure is obtained by the fact that though by the action of hydroxylamine plumbagin yields a dioxime, yet phenylhydrazine and semicarbazide produce only mono-phenylhydrazone and mono-semicarbazone respectively, just in the same way as α-naphthoquinone. By the action of fuming nitric acid plumbagin yields a tetranitro derivative. Bromine in alcohol, chloroform or carbon tetrachloride solution very readily acts on plumbagin forming a dibromo addition product, which points to the unsaturated character of the former.

Plumbagin is a neutral substance. By the action of aqueous or alcoholic ferric chloride it develops a red colour and it dissolves to a cherry-red solution in alkalis. It also gives a dirty green precipitate with alcoholic copper acetate. From these it might be presumed that plumbagin contains one or more phenolic hydroxy groups. This is supported by the fact that by the action of acetyl chloride, benzoyl chloride and ethyl chlorocarbonate, plumbagin in pyridine solution yields the corresponding monoacetyl, monobenzoyl and mocarbethoxy derivatives respectively.

Thus of the five atoms of oxygen present in the plumbagin molecule, three are easily accounted for, namely two in a paraquinone grouping and one in a phenolic hydroxy group. In absence of any methoxy groups, the remaining two oxygen atoms are most probably in a lactone grouping. This assumption is based on the fact that plumbagin has some of the properties of an aromatic lactone like coumarin. Like the latter, an alkaline solution of plumbagin also precipitates a different compound on acidification which gradually reverts to the original plumbagin on standing in contact with mineral acids.

Experimental.

Isolation of Plumbagin.—Air dried roots of *P. rosea* or *zeylanica* are cut to bits of about 5 mm. in length by means of a chopping machine, and then they are exhaustively extracted by means of petroleum ether (b. p. 70°-90°) in a large Sohxlet extractor preferably made of metal. The dark orange-yellow solution on distillation to a small volume and allowing to stand for some time exposed to the air, deposits the crude plumbagin in the form of fine glistening needles of a golden yellow colour. They are then recrystallised several times from dilute alcohol with the addition of animal charcoal, and finally obtained in the form of beautiful silky needles, m. p. 77-78°. (Found: C, 69·1, 68·96; H, 4·8, 4·8; M. W. =296 (cryoscopic in benzene). $C_{11}H_{10}O_3$ requires C, 69·4; H, 4·8 per cent. M.W.=311).

The substance is very soluble in ether, chloroform, acetone, benzene, acetic acid, etc., morderately soluble in hot water and almost insoluble in cold water. It volatilises with steam, and can be sublimed without decomposition on careful heating. It gives a blood-red colour with ferric chloride and a dirty green precipitate

with alcoholic copper acetate. Silver nitrate, lead acetate or calcium chloride does not give any precipitate. It dissolves in concentrated sulphuric acid with a reddish brown colour which changes to violet on warming. It dissolves in caustic alkalis and ammonia with a cherry-red colour at first, but this gradually changes to a reddish brown shade on standing in contact with air probably due to oxidation or hydrolysis. The cherry-red solution on acidification gives a precipitate of the original substance, but the reddish brown solution on similar treatment gives an altogether different product. The substance whether in the solid state or in solution produces blisters very easily in contact with the skin, and even very dilute solutions produce a black stain. The substance reduces Fehling's solution, but not ammoniacal silver nitrate.

Monoacetyl plumbagin, $C_{13}H_{14}O_3 \cdot C_2H_3O$.

Two gms. of plumbagin were dissolved in 10 c.c. of pyridine and 5 c.c. of acetyl chloride gradually added. After the vigorous reaction had subsided the mixture was warmed on the water-bath for a short time and then poured into water. The resulting crystalline brown precipitate was filtered off and recrystallised from dilute alcohol in brownish yellow needles melting at 138°. (Found: C, 67·7 ; H, 5·5. $C_{20}H_{17}O_6$ requires C, 67·9 ; H, 5·09 per cent.).

Monobenzyl plumbagin, $C_{13}H_{14}O_3 \cdot C_7H_5O$.

This was prepared by the action of benzoyl chloride on plumbagin in pyridine solution in a manner exactly similar to the above. It crystallised from dilute alcohol in pale yellow prisms melting at 147°. (Found : C, 71·9 ; H, 4·9. $C_{25}H_{19}O_6$ requires C, 72·2 ; H, 4·5 per cent.).

Monocarbethoxy plumbagin, $C_{13}H_{14}O_3 \cdot C_3H_5O_2$.

This was prepared from plumbagin and ethyl chlorocarbonate in a manner similar to the above. It crystallised from dilute alcohol in yellowish brown needles melting at 109°. (Found: C, 65·3 ; H, 5·3. $C_{21}H_{19}O_7$ requires C, 65·7 ; H, 4·9 per cent.).

Plumbagin-dioxime, $C_{13}H_{13}O_3 : (NOH)_2$.

Two gms. of plumbagin dissolved in 15 c.c. of pyridine were treated with 3 gms. of hydroxylamine hydrochloride and the mixture heated on the water-bath for about half an hour. It was then

poured into water and the resulting crystalline yellow precipitate recrystallised from alcohol in bright yellow needles melting at 220°. It dissolves in sodium hydroxide with a yellow-brown colour. (Found: N, 7·9. $C_{15}H_{17}O_5N_3$ requires N, 8·2 per cent.).

Plumbagin monophenylhydrazone, $C_{18}H_{15}O_4 : N.NH.C_6H_5$.

Two gms. of plumbagin dissolved in 20 c.c. of glacial acetic acid were treated with 3 gms. of phenylhydrazine dissolved in 10 c.c. of the same solvent. The mixture was heated on the water-bath for about an hour and then poured into water. The viscous precipitate was filtered off and crystallised from alcohol with the addition of animal charcoal in fine reddish brown needles melting at 198°. It gives a violet colour with concentrated sulphuric acid and dissolves in organic solvents with a reddish brown colour. (Found: N, 6·5. $C_{24}H_{21}O_4N_3$ requires N, 6·9 per cent.).

Plumbagin monosemicarbazone, $C_{18}H_{15}O_4 : N.NH.CO.NH_2$.

This was prepared from plumbagin and semicarbazide hydrochloride in a manner similar to the dioxime. It crystallises from a mixture of pyridine and alcohol in light brown needles melting above 280°. (Found: N, 11·1. $C_{19}H_{15}O_5N_3$ requires N, 11·4 per cent.).

Action of Potassium Permanganate on Plumbagin.

Five gms. of plumbagin dissolved in dilute sodium hydroxide were treated with a 3 % solution of potassium permanganate in the cold until the latter was no longer decolorised. The precipitated manganese dioxide was filtered off and the filtrate evaporated to a small volume after neutralization with dilute hydrochloric acid. It was then rendered strongly acid with hydrochloric acid when a colourless crystalline precipitate was obtained. The latter melted at 132°, and was identified to be cinnamic acid. The mother-liquor on extraction with ether yielded a further small quantity of cinnamic acid together with traces of benzoic and acetic acids. No other product could be detected.

Action of Fuming Nitric Acid.

Five gms of plumbagin were treated with 25 c.c. of fuming nitric acid in the cold. The substance rapidly dissolved with slight rise of temperature, but no nitrous fumes were evolved. The

mixture was warmed on the water-bath for a short time and then poured into water. The bright yellow precipitate thus obtained was crystallised from alcohol in fine needles melting at 172°, and was found to be a tetranitro derivative. (Found: N, 10·9. $C_{15}H_{11}O_5.(NO_3)_4$ requires N, 11·4 per cent.).

Action of Bromine.—Plumbagin dissolved in alcohol was treated with successive small quantities of bromine and the solution warmed on the water-bath until the bromine was no longer decolorised. The solution was poured into water and the resultant product crystallised from alcohol in bright yellow needles melting at 122°. It was found to be plumbagin dibromide. (Found : Br, 34·4. $C_{15}H_{10}O_5Br_2$ requires Br, 33·9 per cent.).

Distillation with Zinc Dust.—Five gms. of plumbagin were distilled with zinc dust in a current of hydrogen in the manner already described (this *Journal*, 1928, **4**, 28). The distillate which contained both a crystalline substance and a liquid, smelt very strongly of naphthalene. The liquid gave a picrate with picric acid melting at 112°, and was identified to be β-methyl-naphthalene. There was also a small quantity of a brownish tarry substance from which nothing definite could be isolated or identified.

Further work in this direction is in progress.

One of us (A.C.R.) begs to express his best thanks to the authorities of the Kanta Prasad Research Trust for a scholarship which enabled him to take part in this investigation.

Chemical Laboratory,
Allahabad University.

Received May 15, 1928.

Nitro-derivatives of Dibenzylaniline.

By Ranchhodji Dajibhai Desai.

Matzuduira (*Ber.*, 1887, **20**, 1611) prepared *p*-nitrodibenzylaniline by the nitration of dibenzylaniline with fuming nitric acid ($d=1\cdot52$), while by using excess of the same acid, Pinnow and Wiskow (*Ber.*, 1899, **32**, 913) obtained 2 : 4-dinitrodibenzylaniline. It has now been found that under the same conditions, if nitric acid of d 1·48 is used besides the above nitro compounds, very small amounts of *o*-nitrodibenzylaniline and 2 : 6-dinitro-dibenzylaniline respectively are also formed.

The three nitro-dibenzylanilines (*ortho*, *meta*, and *para*-isomers) can be reduced to the corresponding amino derivatives by zinc dust and hydrochloric acid in alcoholic solution, although the *o*-nitro-derivative presents some difficulties. The action of benzaldehyde was studied on *p*- and *m*-amino-dibenzylaniline. From the former, Matzuduira (*loc. cit.*) claims to have isolated a compound melting at 130°, and having the constitution (*p*) $(C_7H_7)_2N.C_6H_4NH.CH(OH).C_6H_5$. Repeating Matzuduira's experiments with scrupulous details, a compound melting at 166-167° was obtained. This proved to be the Schiff's base *p*) $(C_7H_7)_2N\cdot C_6H_4N=CH\cdot C_6H_5$ from the following considerations :—

(1) Estimation of nitrogen, as well as the analysis of the hydrochloride points to the formula $C_{27}H_{24}N_2$ for the base.

(2) The substance is recovered unchanged after heating with phosphorus pentoxide in xylene solution.

(3) The chloroform solution of the base adds up bromine at 0° giving the dibromide. According to Hantzsch (*Ber.*, 1890, **23**, 2773), and James and Judd (*J. Chem. Soc.*, 1914, **105**, 1427), Schiff's bases form dibromides.

From similar considerations, the compounds formed by the action of benzaldehyde on *p*-benzylaminoaniline and *m*-amino-dibenzylaniline are true Schiff's bases and not amino-carbinols.

Experimental.

p-*Nitrodibenzylaniline*.—To a solution of dibenzylaniline (10 gm.) in glacial acetic acid (100 c.c.) cooled to 5°, 3 c.c. of nitric acid (d=1 48) diluted with 25 c.c. of glacial acetic acid were slowly added. Mechanical stirring was used throughout, and the temperature of the solution was not allowed to rise above 10°. After two hours, some *p*-nitrodibenzylaniline that separated out was filtered off, and the solution diluted with water when the nitro compound separated out (yield, 10·5 gm.). The crude product was crystallised from boiling glacial acetic acid, when yellow plates melting at 132-133° were obtained. After removing the solvent, the residue was treated with alcohol. The *p*-nitro-derivative did not go into solution, while the *ortho* compound was left as an oil after removing alcohol completely. Yield of pure *p*-nitro compound=9·5 gm. while that of the *ortho*-derivative is 1 gm.

Synthesis from p-*Nitraniline and Benzyl Chloride*.—A mixture of *p*-nitraniline (14 gm.), benzyl chloride (26 gm.), anhydrous sodium acetate (18 gm.) and iodine (0·2 gm.) was heated on a sand-bath for 12 hours. The mixture was poured into water, and the solid was filtered off. The crude mass was purified by digesting it with xylene (50 c.c.) which removed unaltered *p*-nitraniline and *p*-nitrobenzylaniline. The residue was pure *p*-nitrodibenzylaniline (yield, 65 per cent.).

p-Nitrodibenzylaniline dissolves readily in benzene and acetone, fairly easily in hot glacial acetic acid, less readily in cold glacial acetic acid, and hot alcohol, and is almost insoluble in cold alcohol. It does not form a hydrochloride. It is easily reduced to the corresponding amino compound by zinc dust and hydrochloric acid in alcoholic solution. On dilution with water, the zinc double salt separates out in white needles melting at 200-202°. The base can be liberated by decomposing the salt with alkali. It crystallises from ether in white needles melting at 89-90°, but readily turns brown in air.

The *acetyl derivative* crystallises from alcohol in white plates melting at 137-138°. (Found: N, 8·62. $C_{22}H_{22}ON_2$ requires N, 8.48 per cent.) The *benzoyl derivative* crystallises from glacial acetic acid in white, pointed needles melting at 166°. (Found: N, 7·21. $C_{27}H_{24}ON_2$ requires N, 7·14 per cent.).

Benzylidene-p-dibenzylaminoaniline, $C_6H_5CH{=}NC_6H_4N(C_7H_7)_2$ (*p*).—This is prepared by dissolving the amino compound (1·5 g.) in benzaldahyde (1·5 g.) at 0°. The mixture is washed with alcohol, and the yellow, microcrystalline powder that is obtained is crystallised from benzene when microcrystalline needles melting at 166-167° are obtained. This is readily soluble in chloroform, acetone and glacial acetic acid. Warming with dilute HCl decomposes it into its components. It remains unaffected when heated with phosphorus pentoxide in xylene solution. When heated with acetic anhydride, it gives the acetyl derivative of *p*-aminodibenzylaniline, m.p. 137-138°. (Found: N, 7·52. $C_{29}H_{28}N_2$ requires N, 7·45 per cent.). The *hydrochloride* of the base is prepared by passing HCl into a benzene solution of the base. White plates are obtained when recrystallised from glacial acetic acid. It does not show any definite signs of melting, but sublimes on the sides of the capillary. At about 190°, it turns yellow, but reverts to the original colour on cooling. The hydrochloride is decomposed by hot water. (Found: Cl, 8·72, $C_{28}H_{28}N_2$, HCl requires Cl, 8·6 per cent.).

The *dibromide* is prepared by treating the chloroform solution of the base with bromine in chloroform at 0°. It is a pale-yellow powder soluble in chloroform, benzene and alcohol and melts at 220-225° with decomposition. Heating with alcoholic NaOH decomposes it into benzaldehyde and a product containing bromine. (Found: Br, 29·9. $C_{28}H_{28}N_2Br_2$ requires Br, 29·8 per cent.).

Synthesis of p-*Nitrobenzylaniline*.—This was prepared by heating a mixture of *p*-nitraniline (14 g.), benzyl chloride (13 g.), and anhydrous sodium acetate (9 g.) and 0·2 gm. of iodine in an oil-bath at 125-130° for 8 hours. The mass was poured into water and the solid was filtered off. When crystallised from toluene, tiny, golden-yellow, prismatic needles melting at 147° were obtained. It is easily soluble in benzene, acetone, glacial acetic acid, and ether. The alcoholic solution is easily reduced to the corresponding amino-compound by zinc dust and HCl. The resulting base is an oil, turning brown in air.

The *acetyl derivative* crystallises from alcohol in silky needles melting at 141-142°. (Found: N, 11·9. $C_{15}H_{16}ON_2$ requires N, 11·66 per cent.).

The *benzoyl derivative* crystallises from glacial acetic acid in white plates melting at 182-183°. (Found: N, 9·47. $C_{20}H_{18}ON_2$ requires N, 9·27 per cent.).

Benzylidene-p-benzylaminoaniline.

$C_6H_5CH=N\cdot C_6H_4NH.C_7H_7$ (*p*).

This was prepared by adding 2 g. of the base to 2 g. of benzaldehyde at 0°. After one hour, the mixture was washed with light petrol, and the solid was crystallised from alcohol when pale yellow plates melting at 92-93° were obtained. On heating with dilute HCl, it is decomposed into its components. (Found: N, 10·0. $C_{20}H_{18}N_2$ requires N, 9·8 per cent.).

The *hydrochloride* prepared by the usual method crystallises from glacial acetic acid in stout, white needles, melting at 170-172°, and is readily decomposed by water. (Found: Cl, 10·86. $C_{20}H_{18}N_2$, HCl requires Cl, 10·97 per cent.).

The *dibromide* prepared as above is a yellow, micro-crystalline powder, soluble in chloroform, alcohol, benzene and carbon tetrachloride. It sinters at 200°, and melts at 210° with decomposition. Warm alcoholic KOH decomposes it into benzaldehyde and a brominated compound. (Found: Br, 35·6. $C_{20}H_{18}N_2Br_2$ requires Br, 35·9 per cent.).

Synthesis of o-Nitrodibenzylaniline.

A mixture of *o*-nitraniline (13·8 g.), benzyl chloride (40 g.), anhydrous sodium acetate (17 g.) and iodine (0·2 g.) was heated on a sand-bath for 15 hours. The mixture was steam-distilled to remove excess of benzyl chloride. The residue was extracted with ether, the solution dehydrated with anhydrous sodium sulphate, and ether distilled off. The residue was distilled under reduced pressure, when almost the whole of it distilled away leaving a slight residue of *o*-nitraniline. (yield 20 gms). The distillate solidified when kept in a freezing mixture. It crystallises from light petroleum in yellow plates melting at 32-33°. It is easily soluble in alcohol, acetic acid, acetone, benzene and petroleum. It does not form a hydrochloride. It can be reduced to the corresponding amino compound by zinc dust and HCl, though with difficulty. The resulting base is an oil darkening in air.

The *acetyl derivative* crystallises from alcohol in white needles melting at 121-122°. (Found: N, 8·6. $C_{22}H_{20}ON_2$ requires N, 8·48 per cent.).

The *benzoyl derivative* crystallises from glacial acetic acid in white, prismatic needles melting at 155-156°. (Found: N, 7·2. $C_{27}H_{23}ON_3$ requires N, 7·14 per cent.).

Synthesis of m-*Nitrodibenzylaniline.*

A mixture of *m*-nitraniline (14 g.), benzyl chloride (26 g.), anhydrous sodium acetate (18 g.), and iodine (0·2 g.) was heated at 125-130° for five hours. The product was poured into water, and the oily mass was extracted with ether. The residue did not solidify on keeping in a desiccator, hence concentrated HCl was added. The hydrochloride which separated as a solid was filtered off, and the free base was obtained in a solid condition by decomposing it with NaOH solution (yield, 25 gm.).

The base is soluble in ether, benzene, acetone, toluene, and alcohol. From the latter solvent, it crystallises out in golden-yellow, silky needles melting at 73-74°. (Found: N, 8·88. $C_{20}H_{18}O_2N_2$ requires N, 8·8 per cent.).

The *hydrochloride* crystallises from glacial acetic acid in white prismatic needles, melting at 140-142°. It loses HCl on keeping in a desiccator, and is rapidly decomposed by water. (Found: Cl, 10·1. $C_{20}H_{18}O_2N_2$, HCl requires Cl, 10·0 per cent.).

m-*Aminodibenzylaniline* was obtained by reducing the nitro compound with zinc dust and HCl. The free base is an oil which is oxidised by air.

The *acetyl derivative* crystallises from alcohol in white, slender needles melting at 143-144°.

The *benzoyl derivative* crystallises from glacial acetic acid in prismatic needles melting at 171-172°. (Found: N, 7·25. $C_{27}H_{23}ON_3$ requires N, 7·14 per cent.).

Benzylidene-m-*dibenzylaminoaniline.*

This was prepared by adding 1·5 gm. of the base to 1·5 gm. of benzaldehyde at 0°. After washing the mixture with dilute alcohol, the yellow solid was crystallised from benzene when yellow, microscopic plates, m. p. 156-158° were obtained. It is decomposed into its components by warm, dilute hydrochloric acid. (Found: N, 7·55. $C_{27}H_{24}N_2$ requires N, 7·45 per cent.).

The *hydrochloride* prepared as usual melts at 195° with decomposition. It is easily decomposed by water, (Found: Cl, 8·7. $C_{27}H_{24}N_2$, HCl requires Cl, 8·6 per cent.).

The *dibromide* was prepared as usual. It is a yellow powder melting at 196-198° with decomposition. (Found: Br, 30·0. $C_{27}H_{24}N_2Br_2$ requires Br, 29·8 per cent.).

2:4-*Dinitro-dibenzylaniline* and 2:6-*Dinitro-dibenzylaniline*.

To a solution of dibenzylaniline (10 g.) in glacial acetic acid (100 c.c.) 10 c.c. of nitric acid (*d* 1·48) diluted with 25 c.c. of glacial acetic acid were slowly added. Mechanical stirring was kept throughout, and the temperature was kept at 15-20°. After nearly three hours, lemon-yellow prismatic needles began to separate. After filtering off the solid, the solution was freely diluted with water when the nitro compound separated as a yellow powder (yield, 11·0 gm.). The crude mass was dissolved in 50 c.c. of boiling glacial acetic acid, and on cooling, pure crystals of 2:4-dinitrodibenzylaniline were obtained. This substance melts at 103-104° and not at 106° as given by Pinnow and Wiskow (*loc. cit.*). On concentrating the mother-liquor, a further amount of the same product was obtained. The mother-liquor was reduced to one-third of its original bulk. Spontaneous crystallisation gave two types of crystals, *viz.* lemon-yellow, prismatic needles and orange-yellow, stout, pointed, prismatic needles. The latter were mechanically separated by forceps, and melted at 107°. This is the new nitro derivative which has been shown to be 2:6-dinitro-dibenzylaniline. The yield of this compound is very small (0·5 gm.).

2:4-*Dinitro-dibenzylaniline* is sparingly soluble in ether, but readily in hot glacial acetic acid. (Found: N, 11·78. $C_{20}H_{17}O_4N_3$ requires N, 11·57 per cent.).

Decomposition of 2:4-*Dinitrodibenzylaniline*.

One gm. of the compound was heated with 5 c.c. of acetic anhydride and 1 c.c. of concentrated hydrochloric acid for two hours under reflux. On pouring the mixture into water, a yellow powder was obtained, and the filtrate smelt of benzyl chloride. Recrystallisation of the crude product from glacial acetic acid gave fine yellow needles melting at 116°. (Found: N, 15·5. $C_{13}H_{11}O_4N_3$ requires N, 15·4 per cent.). This is 2:4-dinitrobenzylaniline synthesised by Mulder (*Rec. trav. chim.*, 1906, **25**, 108).

In another experiment, the heating of the above mixture was carried out in a sealed tube at 145-150° for 8 hours. A heavy oil settled at the bottom when the mixture was poured into water, This was removed by extraction with ether, and then acetylated as usual. The solid, on crystallisation from alcohol, gave pale-white needles melting at 120°. This is the acetyl derivative of 2:4-dinitraniline (Rudnew, *Zeit. Chem.*, 1871, 202). (Found: N, 18·8. $C_8H_7O_5N_3$ requires N, 18·66 per cent.).

2:6-Dinitro-dibenzylaniline.

The method of isolating this substance has already been described. It dissolves easily in acetic acid, acetone and benzene, but sparingly in alcohol. It melts at 107°, and when mixed with 2:4-dinitro-dibenzylaniline, the m.p. is lowered to 85-90°. (Found: N, 11·68. $C_{20}H_{17}O_4N_3$ requires N, 11·57 per cent.).

Decomposition of 2:6-Dinitro-dibenzylaniline.

0·3 Gm. was heated with 3 c.c. of acetic anhydride and 1 c.c. of conc. HCl for two hours, under reflux. When the mixture was poured into water, a strong smell of benzyl chloride was perceptible, and a solid was obtained. When crystallised from alcohol, yellow needles melting at 138° were obtained. This gave all the tests for 2:6-dinitraniline (Hoff, *Annalen*, 1900 **311**, 108; Salkowsky, *ibid*, 1874 **174**, 237). (Found: N, 23·1. $C_6H_5O_4N_3$ requires N, 22·95 per cent.).

This reaction establishes the constitution of the original dinitro compound melting at 107° as 2:6-dinitrophenyldibenzylamine (2:6) $(NO_2)_2C_6H_3N(C_7H_7)_2$ (1).

The work described in this communication was carried out at the Royal Institute of Science, Bombay, and the author takes this opportunity of expressing his thanks to Dr. A. N. Meldrum for his sympathy and encouragement, and for giving full access to the resources of the laboratory.

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Alkali Sulphonates of Coumarin and Nitrocoumarin.

By Rajendra Nath Sen and Duhkhaharan Chakravarti.

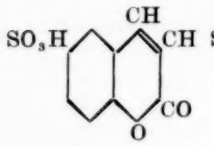
Perkin (*J. Chem. Soc.*, 1873, **24**, 37) sulphonated coumarin with fuming sulphuric acid and obtained mono-sulphonic acid of coumarin (sulphocoumarilic acid) at the temperature of water-bath, and the disulphonic acid (disulphocoumarilic acid) at 150° ; but he did not determine the position of the sulphonic acid groups. The object of the present paper is to study further the sulphonation of coumarin and nitrocoumarin with a view to determine the constitution of these sulphonic acids and also to prepare their simple derivatives such as the sulphochlorides and the sulphonamides.

The mono-sulphonic acid of coumarin has been prepared by the action of ordinary fuming sulphuric acid on coumarin on the water-bath and the disulphonic acid and nitrocoumarin monosulphonic acid have been obtained by the action of fuming sulphuric acid on coumarin and nitrocoumarin respectively at 150°. The laborious method of isolation of the sulphonic acids of coumarin followed by Perkin by means of their barium salts has been replaced by the salting out process with advantage, whereby they are readily obtained in good yields as their sodium salts. The yield of the disulphonic acid of coumarin is much greater with 50% fuming sulphuric acid than with ordinary fuming acid used by Perkin.

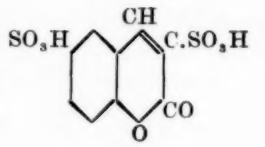
The usual methods for the determination of the position of the sulphonic acid groups in simpler aromatic compounds by the replacement of the sulphonic acid group by hydroxyl group by alkali-fusion or by nitro group (*J. Am. Chem. Soc.*, 1919, **41**, 2039) or halogen atoms (*ibid*, page 2028) have not been successful in the case of the sulphonic acids of coumarin the alkali fusion leading to a rupture of the lactonic ring of the coumarin molecule.

The constitution of these acids has therefore been determined by oxidising the lactonic ring with alkaline potassium permanganate solution and obtaining from each of them known derivatives of salicylic acid. Thus the oxidation product of the mono-sulphonic acid of coumarin or sulpho-coumarilic acid of Perkin melts at 113°,

the desiccated product shrinks above 115°, and decomposes at about 178° and has there- fore been identified with 5-sulpho-salicylic acid (Meldrum and Shah, *J. Chem. Soc.*, 1923, **123**, 1989) proving it to be coumarin-6-sul- phonic acid (I).



(I)



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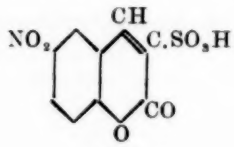

(III)

It has been shewn by Clayton (*J. Chem. Soc.*, 1910, **97** 1397) that when 6-nitrocoumarin is further nitrated, the second nitro group enters the lactonic ring in preference to the benzenoid ring and this peculiar susceptibility of the lactonic ring has also been observed in the case of sulphonation. Thus 6-nitrocoumarin-sulphonic acid gives on oxidation 5 nitrosalicylic acid (m. p. 228°), shewing that the SO_3H group has entered the lactone ring. Similarly in the case of the disulphonic acid of coumarin, the second sulphonic acid group enters the lactone ring as the oxidation product (5-sulphosalicylic acid) contains only one sulphonic acid group.

It has been definitely proved by Clayton (*loc. cit.*) that the nitration product of 6-nitrocoumarin is 3 : 6-dinitrocoumarin and from analogy it seems reasonable to suppose that the SO_3H group entering the lactonic ring like the nitro group occupies the position 3, and hence the disulphonic acid of coumarin or the disulpho-coumarilic acid of Perkin is presumably coumarin 3 : 6-disulphonic acid (II) and the nitro-coumarin sulphonic acid is coumarin-6-nitro-3-sulphonic acid (III).

These sulphonic acids, readily isolated as their sodium salts by salting out, yield with PCl_5 or $POCl_3$ sulphochlorides, which in their turn give sulphonamides and sulphonanilides on usual treatment with ammonium carbonate and aniline. These sulphochlorides and sulphonamides are crystalline substances with definite melting points.

Experimental.

Sodium salt of Coumarin-6-sulphonic Acid.—Coumarin (10 g.) and ordinary fuming sulphuric acid (50 g.) are heated on the boiling water-bath for two hours and the cold solution is filtered into

saturated brine and on keeping for a day or two the whole mass solidifies. The solution is filtered off and the residue washed with brine and finally crystallised from water (yield 85 %).

It forms thin silky needles, readily soluble in water and sparingly soluble in alcohol. (Found: S, 12·6, 12·65. $C_9H_5O_5SNa$ requires S, 12·9 per cent.).

Coumarin-6-sulphochloride.—The above sodium salt is mixed with PCl_5 or $POCl_3$ and heated on the water-bath for an hour. The mixture is poured into ice and filtered. The residue is washed with water and extracted with ether. Crystalline solid, soluble in ether and chloroform; m. p. 115°. (Found: S, 13·05. $C_9H_5O_4SCl$ requires S, 13·1 per cent.).

Coumarin-6-sulphonamide.—The sulphochloride is thoroughly mixed with excess of ammonium carbonate and heated on the water-bath for about 2 hours. The mixture is then washed with water and the residue crystallised from water. Needle-shaped crystals, soluble in alcohol and boiling water; m. p. 186°. (Found: S, 14·0; N, 6·3. $C_9H_7O_4SN$ requires S, 14·2; N, 6·2 per cent.).

Sulphonanilide.—The sulphochloride is dissolved in hot aniline and the solution heated on the water-bath for a few minutes. The solution is then poured into acid water, when the anilide is precipitated. It is filtered, washed with acid water and finally crystallised from dilute alcohol. Needle-shaped crystalline solid, insoluble in water and easily soluble in alcohol; m. p. 132°. (Found: S, 10·68; N, 4·8. $C_{15}H_{11}O_4SN$ requires S, 10·6; N, 4·6 per cent.).

Oxidation of Sodium Salt of Coumarin-6-sulphonic Acid.—Five gm. of the substance are dissolved in 2N-KOH and a 4 per cent. solution of potassium permanganate is added drop by drop to the alkaline solution cooled to 0° till the oxidation is complete. The solution is then heated for about an hour on the water-bath and then filtered from the thick mud of precipitated manganese dioxide. The filtrate is then concentrated on the water-bath and conc. HCl added, when crystals of the acid potassium salt of 5-sulphosalicylic acid separate. These are filtered off and recrystallised from water. (Found: S, 12·8; K, 15·4. $C_7H_5O_6SK$ requires S, 12·5; K, 15·2 per cent.).

The acid potassium salt is dissolved in dilute alcohol and barium chloride solution is added to it, when barium salt of 5-sulphosali-

cylic acid separates. This is filtered off, dissolved in water, and decomposed with theoretical quantity of sulphuric acid, and the solution, after being filtered off from the precipitated barium sulphate, is concentrated on the water-bath and left in a desiccator overnight, when crystals of 5-sulphosalicylic acid separate. Recrystallised from water, the product melts at 118°, shrinks from about 115° and decomposes at about 178°.

Disodium Salt of Coumarin-3:6-disulphonic Acid.—Ten gms. of coumarin and 70 gms. of 50% fuming sulphuric acid are heated on an oil-bath at 150° for three to four hours and the cold solution is filtered into saturated brine, when the mass solidifies all at once. The solution is filtered off and the residue, containing a mixture of the mono- and di-sulphonic acids of coumarin, is thoroughly washed with brine and crystallised three or four times from water, when the more soluble salt of mono-sulphonic acid remains in solution and the less soluble salt of the disulphonic acid is obtained in the pure state (yield—07 per cent.).

Silky needles, moderately soluble in water and almost insoluble in alcohol. (Found: S, 17·9, 18·0. $C_9H_4O_8S_2Na_2$ requires S, 18·3 per cent.).

Disulpho-dichloride.—Prepared as in the case of mono-sulphochloride. Needle-shaped crystals, soluble in ether and benzene, moderately soluble in alcohol and insoluble in water ; m. p. 170°-173°. (Found: S, 18·65. $C_9H_4O_6S_2Cl_2$ requires S, 18·7 per cent.).

Disulphon-diamide.—Prepared as in the case of mono-sulphonamide and is crystallised from water. Needle-shaped crystals, soluble in ether and alcohol and somewhat soluble in water, m. p. above 240°. (Found: N, 9·15. $C_9H_8O_6S_2N_2$ requires N, 9·2 per cent.).

Di-sulphondianilide.—Prepared as in the case of the mono-sulphonanilide and is crystallised from dilute alcohol. Yellow crystals soluble in alcohol and is insoluble in water. (Found: N, 6·1. $C_{21}H_{16}O_6S_2N_2$ requires N, 6·1 per cent.).

Oxidation of Coumarin-3:6-disulphonic Acid.—The process of oxidation is the same as in the case of the mono-sulphonic acid and the acid potassium salt of 5-sulphosalicylic acid is obtained in good

yield. (Found: S, 12·9 ; K, 15·3. $C_7H_3O_6SK$ requires S, 12·5 ; K, 15·2 per cent.).

Sodium salt of Coumarin-6-nitro-3-sulphonic Acid.—Ten gms. of 6-nitrocoumarin and 60 gms. of 50% fuming sulphuric acid are heated on the oil-bath at 150° for three to four hours and the cold solution is filtered into saturated brine, when crystals of the sodium salt separate. These are filtered off, washed with brine and recrystallised from water (yield—80 per cent.).

Long yellowish needles, moderately soluble in alcohol and easily soluble in water. (Found: S, 10·7 ; N, 4·85. $C_9H_4O_7SNNa$ requires S, 10·9; N, 4·8 per cent.).

The *sulphochloride* was prepared as in the case of the mono-sulphochloride and then crystallised from benzene. Crystalline solid, readily soluble in alcohol, moderately soluble in benzene and almost insoluble in ether ; m. p. 205°. (Found: S, 11·2 ; N, 4·8. $C_9H_4O_6SNCl$ requires S, 11·1; N, 4·8 per cent.).

Sulphonamide.—Prepared as in the case of the mono-sulphonamide and is then crystallised from water. Needle-shaped crystals, readily soluble in alcohol and boiling water. Does not melt up to 260°. (Found: N, 10·2. $C_9H_6O_6SN_2$ requires N, 10·4 per cent.).

Sulphonanilide.—Prepared as in the case of the mono-sulphonanilide and then crystallised from alcohol. Crystalline solid, soluble in alcohol and insoluble in water ; m. p 130°. (Found: N, 8·3. $C_{15}H_{10}O_6SN_2$ requires N, 8·1 per cent.).

Oxidation of Coumarin-6-nitro-3-sulphonic Acid.—The process of oxidation is the same as in the case of the mono- and di-sulphonic acids. Conc. hydrochloric acid when added to the concentrated alkaline solution after the removal of the precipitated manganese dioxide throws down crystals of 5-nitrosalicylic acid. The product, after recrystallisation from water, melts at 228°.

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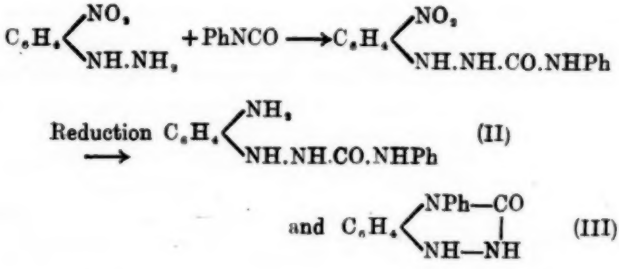
o-Aminophenylhydrazine and some Interesting Heterocyclic Compounds Derived from it. Part IV.

Lengthened *o*-Diderivatives of Benzene and their Ring-closure.

By Praphulla Chandra Guha and Teje ndra Nath Ghosh.

In Part III (*J. Indian Chem. Soc.*, 1927, **4**, 561) the reaction of *o*-aminophenyl-4R-thiosemicarbazides with thiocarbimides, carbimides, potassium cyanate and thiocyanate, aldehydes etc. and the behaviour of the compounds thus obtained towards different types of ring-closing agents have been described. In this part the action of *iso*cyanates, *iso*thiocyanates, aldehydes, ferric chloride and hydrazine hydrate, etc. upon aminophenylsemicarbazides as also the ring closure of some of the lengthened *o*-diderivatives of benzene by the action of hydrochloric acid, etc., and also the ring-closure of some typical derivatives of *o*-nitrophenylhydrazine on reduction will be described.

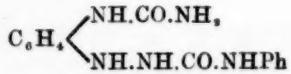
o-Nitrophenylhydrazine reacts with phenyl cyanate to yield *o* nitrophenyl-4-phenylsemicarbazide (I) which in its turn gives two products on reduction, one being 1-*o*-aminophenyl-4-phenylsemicarbazide (II) and the other 1-phenyl-2:3-benzo-6-keto-1:4:5-triazine (III).



Evidently, the triazine (III) is formed from 1-aminophenyl-4-phenylsemicarbazide (II) by the loss of one molecule of ammonia in presence of strong hydrochloric acid. This view gets additional

support from the fact that the amino compound on treatment with acetic anhydride or with strong hydrochloric acid has been found to yield the same benzo-triazine compound.

1-*o*-Aminophenyl-4-phenylsemicarbazide redily reacts with potassium cyanate, phenyl*iso*cyanate, phenyl mu tard oil and *o*-nitrobenzaldehyde to yield respectively 1-carbamido-2-phenyl semicarbazido-benzene (IV), 1-phenylcarbamido 2-phenylsemicarbaz ido-benzene (V), 1-phenyl-thiocarbamido-2-phenylsemicarbazido-ban zene (VI) and 1-nitrobenzalanilido-2-phenylsemicarbazido-benzene (VII):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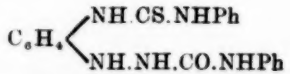
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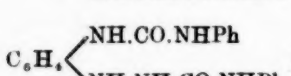
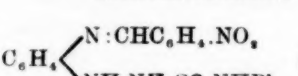

(V)

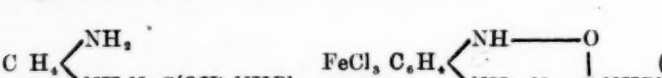

(VII)

The first of the above four compounds loses a molecule of water on being treated with strong hydrochloric acid yielding 2:3-benzo-6-phenylamino-8-keto-1:4:5:7 octatetrazine (VIII).

(VIII)

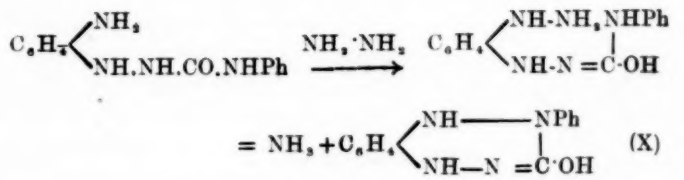
and is identical with the compound obtained from 1-carbamido-2-phenylthiosemicarbazido-benzene by the action of the same reagent (Part III, page 570).

Ferric chloride exerts its oxidising action upon 1-*o*-aminophenyl-4-phenylsemicarbazide similarly as in the case of the corresponding thio compounds, to yield 3:4-benzo-7-phenylamino-1:2:5:6-oxheptatriazine (IX), thus:


(IX)

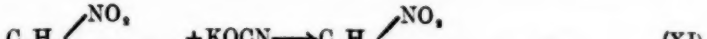
Stolle (*J. pr. Chem.*, 1903, **68**, 137; 1904, **70**, 395, 414) similarly obtained oxbiazole derivatives by oxidising acylhydrazones of aldehydes.

Hydrazine hydrate reacts with 1-*o*-aminophenyl-4-phenylsemicarbazide exactly in the same manner as has been observed with the corresponding thio compound (Part III. page 571) to yield 1-N-phenyl-3:4-benzo-7-hydroxy-1:2:5:6-heptatetrazine (X), thus:



(X)

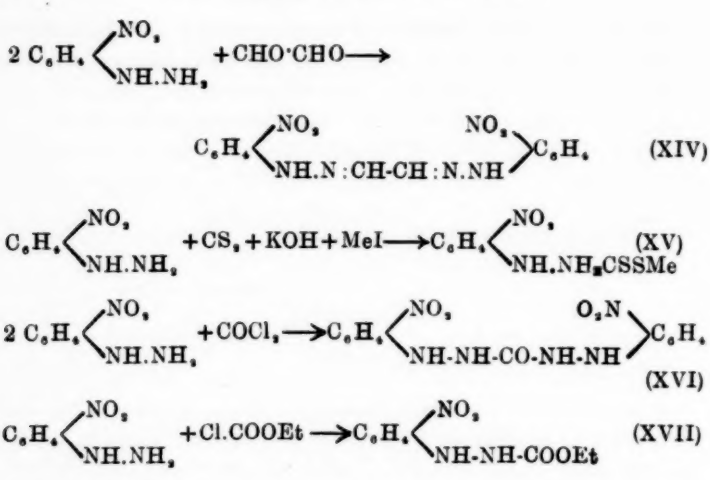
Formation of hetero-cyclic compounds from suitable *ortho*-nitro derivatives of benzene by reduction is well known. Paal (*Ber.*, 1891, **24**, 959, 3059) and Busch (*Ber.*, 1894, **27**, 2899) prepared N-phenyl-iminazoles by reducing *o*-nitro-benzylanilines and Hobrecker (*Ber.*, 1872, **5**, 920) prepared benziminazole by reducing *o*-nitroacetanilide. Guha and De prepared a large number of poly-hetero-atomic compounds by reducing *o*-nitro-(also hydroxy)-benzaldehyde-*o*-nitrophenylhydrazones, *o*-nitrophenylhydrazones of 1:2-diketones and *o*:*o'*-nitro-amino-diphenyl-hydrazine (*J. Indian Chem. Soc.*, 1926, **3**, 41). *o*-Nitro-phenylhydrazine has now been made to react with potassium cyanate, potassium thiocyanate, *o*-chlorobenzaldehyde, glyoxal, carbondisulphide and methyl iodide in presence of potassium hydroxide, carbonyl chloride, ethyl chloroformate, etc., to yield 1-*o*-nitrophenyl-semicarbazide (XI), 1-*o*-nitrophenyl-thiosemicarbazide (XII), *o*-chlorobenzaldehyde-*o*-nitrophenylhydrazone (XIII), glyoxal-*o*-nitrophenylosazone (XIV), *o*-nitrophenyl-methyl-dithiocarbazinate (XV), di-*o*-nitrophenyl-carbohydrazide (XVI) and ethyl-*o*-nitrophenylcarbazinate (XVII) respectively, thus:—



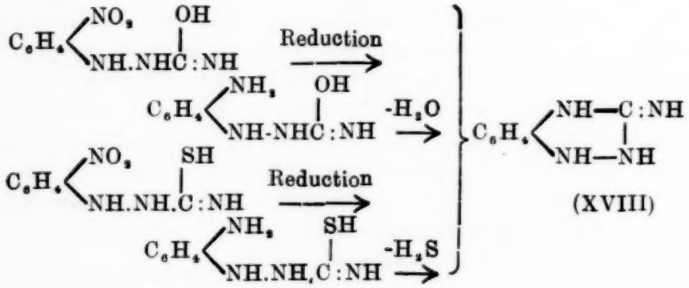
(XI)

(XII)

(XIII)



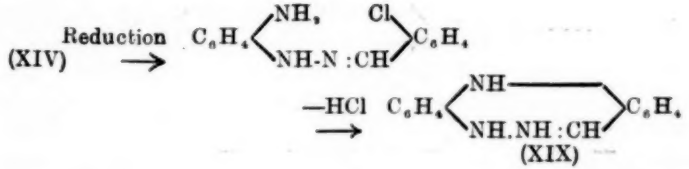
Both the compounds (XI) and (XII) on reduction with tin and hydrochloric acid give the same benzo-triazine derivative (XVIII), by losing one molecule of water and sulphuretted hydrogen respectively from the intermediate aminophenyl-semicarbazide and aminophenyl-thiosemicarbazide, thus :—



It is noteworthy that the intermediate amino-compounds formed in the first stage of the reduction processes cannot be isolated; (compare the simultaneous formation and isolation of the amino-compounds II, IV, VIII of Part III). This shows that the *o*-aminophenyl-semicarbazide and *o*-aminophenyl-thiosemicarbazide possess a greater tendency to form ring-closed compounds in presence of hydrochloric acid than compounds in which the $CONH_2$ and $CSNH_2$ groups are substituted. Another point of considerable significance is that the end carbonamide ($CONH_2$) and thiocarbonamide ($CSNH_2$)

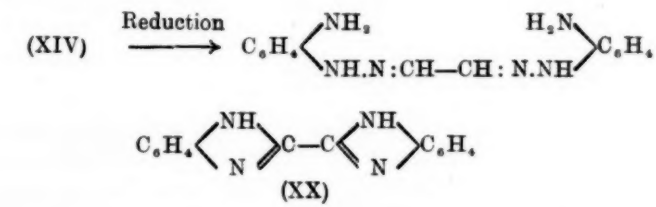
groupings being unsubstituted, the nature of ring-closure differs remarkably from that observed in the formation of compound III (also of III and VI of Part III) where the carbonamide groupings are substituted: in the former case the ring closure is effected with the elimination of water or sulphuretted hydrogen and in the latter with the elimination of ammonia.

o-Chlorobenzaldehyde-nitrophenylhydrazone (XIII) on reduction furnishes the unstable amino-compound from which 2:3:7:8-dibenzo-1:4:5-octatriazine (XIX) is formed by the loss of one molecule of hydrochloric acid, thus:



(XIX)

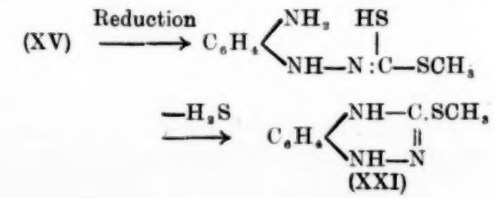
Glyoxal-nitrophenylosazone (XIV) on reduction gives similarly as the mono μ-benziminazole formation of Guha and Ray (*J. Indian Chem. Soc.*, 1926, **3**, 86) the bis-benziminazole compound (XX), thus:



(XX)

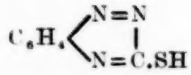
Bis-benziminazole was prepared by Hubner (*Annalen*, 1881, **209**, 339) by reducing *o*-nitro-oxanilides.

o-Nitrophenyl-methyl-dithiocarbazinate (XV) on reduction forms the unstable amino compound which loses a molecule of sulphuretted hydrogen to yield methylthiol-benzotriazine (XXI), thus:

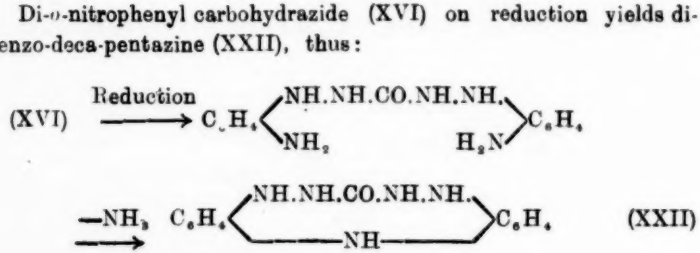


(XXI)

Arndt and Rosenau (*Ber.*, 1917, **50**, 1248) prepared μ-phentriazoxine-mercaptan by the action of alkali upon *o*-nitrophenylthiourea and by reducing it with zinc dust and alkali obtained 3-phentriazine mercaptan of the formula,



Di-*o*-nitrophenyl carbohydrazide (XVI) on reduction yields dibenzo-deca-pentazine (XXII), thus:



For similar poly-hetero-ring formations, compare Thiele and Holzinger (*Annalen*, 1899, **305**, 100) and Duval (*Bull. Soc. Chim.*, 1910, **7**, 730) who prepared imino-dibenzyl by heating 2:2′-diamino-dibenzyl and azo-diphenylethane by reducing 2:2′-dinitro-diphenyl-ethane with zinc dust in presence of aqueous alcoholic baryta.

Experimental.

o-*Nitrophenyl*-4-*phenylsemicarbazide* (I).—Phenylisocyanate (3·5 g.) was added slowly under shaking to an aqueous solution of *o*-nitrophenylhydrazine hydrochloride (5 g.). The reaction took place at once with the evolution of heat and frothing and the separation of a yellow precipitate which was filtered, washed with water and crystallised from alcohol in beautiful yellow plates, m.p. 202°. It is soluble in acetone, pyridine, acetic acid, sparingly soluble in cold water but readily soluble in hot water. (Found: N, 20·47. $C_{13}H_{12}O_3N_4$ requires N, 20·58 per cent.).

Reduction of o-*Nitrophenyl-semicarbazide*: *Formation of* 1-o-*Amino-phenyl*-4-*phenylsemicarbazide* (II) *and* 1-*Phenyl*-2:3-*benzo*-6-*keto*-1:4:5-*triazine* (III).—The semicarbazide (5 g.) was heated with granulated tin (15 g.) and concentrated hydrochloric acid (100 c.c.) on a water-bath under reflux for 2-3 hours when a clear yellow solution was obtained. The solution was further heated on a

water-bath for about an hour more when the solution became quite colourless. The solution after cooling was diluted with about 150 c.c. water when a white solid (*i*) separated out, the filtered solution (*ii*) was kept for further treatment.

Isolation of Compound (III).—The white solid (*i*) was crystallised from dilute alcohol in beautiful white prisms, m.p. 170-171°. It is soluble in hot water and in cold dilute alkali (yield, 0·7 gm.). (Found: N, 18·52. $C_{13}H_{11}ON_3$ requires N, 18·66 per cent.).

Isolation of Compound (II).—The clear filtrate (*ii*) was largely diluted with water and tin was removed by passing sulphuretted hydrogen and the filtered solution was evaporated almost to dryness on the water-bath when reddish brown crystals were obtained. The compound was further purified by adding ether to an alcoholic solution of the substance and the white shining crystalline mass thus obtained was finally recrystallised from dilute alcohol, m.p. 250-251° with decomposition producing a blue colouration after darkening at 210°. It changes to reddish brown on standing. It is highly soluble in water and gives a red azo-dye on diazotisation and coupling with β-naphthol. (Found: N, 20·39. $C_{13}H_{14}ON_4$,HCl requires N, 20·14 per cent.).

The free Base.—One gram of the above hydrochloride was dissolved in the least quantity of water and ammonia added drop by drop until just alkaline. A brownish precipitate separated out which was, after filtration and washing with water, crystallised from alcohol in brownish needles, m.p. 145°. (Found : N, 23·27. $C_{13}H_{14}ON_4$ requires N, 23·14 per cent.).

Action of Acetic Anhydride upon 1-*o*-*Aminophenyl*-4-*phenylsemicarbazide.*—The semicarbazide hydrochloride (1 g.) was heated with acetic anhydride (3 c.c.) on a sand-bath under reflux for about 20 minutes and the clear solution was poured into water when a brownish white crystalline mass separated out. A second crop was obtained by concentrating the solution. On crystallisation from dilute alcohol it yielded white shining prisms, m.p. 170-171° (yield, 0·4 gm.). (Found: N, 18·59. $C_{13}H_{11}ON_3$ requires N, 18·66 per cent.). The compound is evidently identical with compound (III) which was also proved by taking the mixed melting point.

1-*Phenylcarbamido*-2-*phenylsemicarbazido-benzene* (V).—Phenyl *iso*cyanate (0·5 g.) was added drop by drop to 1-*o*-aminophenyl-4-phenylsemicarbazide hydrochloride (1 g.) dissolved in the smallest

quantity of water under constant stirring when a brownish white precipitate separated out. It was crystallised from alcohol in white shining rectangular plates, m.p. above 290°. (Found: N. 19·45. $C_{20}H_{16}O_2N_8$ requires N, 19·39 per cent.).

1-*Carbamido*-2-*phenylsemicarbazido*-*benzene* (IV).—Potassium cyanate (0·6 g.) dissolved in the smallest quantity of water was added drop by drop under cooling to 1-*o*-aminophenyl-4-phenylsemicarbazide hydrochloride (2 g.) also dissolved in the smallest quantity of water. A white solid came out at once which was filtered, washed with water and was finally crystallised from dilute alcohol as white plates which did not melt even at 290°. It is soluble in hot water and in cold alkali. (Found: N, 24·52. $C_{14}H_{12}O_2N_8$ requires N, 24·56 per cent.).

Action of strong Hydrochloric Acid upon Compound (IV) : *Formation of* 2:3-*Benzo*-6-*phenylamino*-8-*keto*-1:4:5:7-*octatetrazine* (VIII). —Two gm. of the above compound (IV) was heated with 100 c.c. of hydrochloric acid (*d* 1·19) for about an hour and the clear solution thus obtained was poured into water when a shining white crystalline mass was obtained. A second crop was obtained by evaporating the mother-liquor. It was finally crystallised from dilute alcohol in white plates, m.p. 145-146° (yield, 1·2 gm.). (Found: N, 26·06. $C_{14}H_{12}ON_8$ requires N, 26·22 per cent.). The identity of this substance with compound XVII of Part III was proved by taking a mixed melting point.

1-*Phenylthiocarbamido*-2-*phenylsemicarbazido*-*benzene* (VI).—An alcoholic solution of 1-*o*-aminophenyl-4-phenylsemicarbazide (1 g.) and phenyl mustard oil (0·5 g.) was heated under reflux on a water-bath for 2-3 hours. The reaction product was then poured into water when a brownish white mass separated out which was crystallised from dilute alcohol as brownish white plates, m.p. above 290°. It is soluble in hot water and in cold concentrated alkali (yield, 1·2 gm.) (Found: N, 18·63. $C_{20}H_{16}ON_8S$ requires N, 18·57 per cent.).

1-*o*-*Nitrobenzalanilido*-2-*phenylsemicarbazido*-*benzene* (VII).—An alcoholic solution of 1-*o*-aminophenyl-2-phenylsemicarbazide hydrochloride (1 g.) and *o*-nitrobenzaldehyde (0·5 g.) was heated under reflux for about an hour. The clear solution on cooling gave a crystalline product which after filtration under pump and washing with a small quantity of cold alcohol was crystallised from alcohol,

m. p. 245-246° (yield, 0·6 gm.). (Found: N, 18·24. $C_{20}H_{17}O_3N_5$ requires N, 18·67 per cent.).

Action of Ferric Chloride upon (II): *Formation of* 3:4-*Benzo*-7-*phenylamino*-1:2:5:6-*oxheptatriazine* (IX).—The method of preparation was the same as that of the compound (XVIII) of Part III. The hydrochloride was crystallised from water slightly acidulated with hydrochloric acid in beautiful reddish brown needles which did not melt even at 290°. (Found: N, 20·12. $C_{13}H_{11}ON_4,HCl$ requires N, 20·29 per cent.).

Action of Hydrazine Hydrate upon 1-o-*Aminophenyl*-4-*phenyl semicarbazide*: *Formation of* 1-N-*Phenyl*-3:4-*benzo*-7-*hydroxy*-1:4:5:6-*heptatetrazine* (X).—An alcoholic solution of 1-*o*-aminophenyl-4-phenyl semicarbazide (2 g.) and hydrazine hydrate (0·4 g.) were heated under reflux for about forty minutes. The solution on cooling gave a brownish white crystalline mass which was filtered, washed successively with alcohol and water and crystallised from dilute alcohol in colourless shining needles, m. p. 90-91°. It is soluble in hot water and cold dilute alkali. (Found: N, 23·02. $C_{13}H_{12}ON_4$ requires N, 23·33 per cent.).

o-*Nitrophenyl semicarbazide* (XI).—An aqueous solution of potassium cyanate (1 g.) was drop by added drop under cooling to a very concentrated solution of *o*-nitrophenylhydrazine hydrochloride (2 g.). The reaction took place instantaneously and a yellow solid was soon precipitated which was purified by dissolving in the minimum quantity of hot alcohol and scratching the sides of the containing vessel when cold. The fine yellow crystalline powder melted at 225° with decomposition. It is sparingly soluble in hot water but readily soluble in acetic acid and pyridine. (Found: N, 28·49. $C_7H_8O_3N_4$ requires N, 28·57 per cent.).

Reduction of Compound (XI): *Formation of* 2:3-*Benzo*-5-*imino*-1:4:6-*triazine* (XVIII).—*o*-Nitrophenyl semicarbazide (5 g.) was heated with granulated tin (10 g.) and concentrated hydrochloric acid (60 c. c.) in a flask fitted with an upright condenser. After an hour, a light yellow clear solution was obtained which, however, became colourless on further heating. The solution was then largely diluted with water and tin removed by sulphuretted hydrogen. The solution was then evaporated almost to dryness on the water-bath and the reddish-brown crystalline residue thus obtained was further purified by crystallisation from water slightly acidulated with hydrochloric acid in brownish white prisms, m. p. 248-249°

with decomposition and producing a blue colouration. It turns reddish brown on standing for a few days and gives silver chloride with silver nitrate solution.

The free Base.—The above hydrochloride (0·5 g.) was dissolved in the minimum quantity of water and the requisite quantity of ammonia added to it, when a yellowish white flocculent precipitate was obtained. It was filtered, washed with water and crystallised from dilute alcohol, m. p. 85°. It is readily soluble in water. (Found: N, 37·61. $C_7H_8N_4$ requires N, 37·84 per cent.).

The Acetyl Derivative.—0·5 Gm. of the compound (XVIII) was heated with 3 c.c. of acetic anhydride for about 15 minutes when a clear solution was obtained. On cooling, the solution gave a brownish white crystalline mass which was crystallised from acetic acid in needles, m. p. 182-183°.

1-o-*Nitrophenylthiosemicarbazide* (XII).—Potassium sulphocyanide (3 g.) dissolved in the smallest quantity of water was added slowly under cooling to an aqueous solution of *o*-nitrophenylhydrazine hydrochloride (5 g.). The reaction took place at once: however, for completion of the reaction, the mixture was heated on the water-bath for about an hour. The light yellow precipitate thus obtained was crystallised from hot water in light yellow needles m. p. 200° with decomposition; yield, 5 gms. (Found: S, 15·41. $C_7H_8O_2N_4S$ requires S, 15·09 per cent.).

Reduction of 1-o-*Nitrophenylthiosemicarbazide* : *Formation of* 2 : 3-*Benzo*-5-*imino*-1 : 4 : 6-*triazine* (XVIII).—The method of procedure was the same as adopted for the reduction of compound (XI). The hydrochloride was crystallised from alcohol in brownish white prisms, m.p. 248-249° with decomposition. It turns reddish brown on standing for a few days and gives silver chloride with silver nitrate solution. (Found : N, 16·69 ; Cl, 42·83. $C_7H_8N_4$, 4HCl, $2H_2O$ requires N, 16·97 ; Cl, 43·03 per cent.). It gave the free basic compound melting at 85°.

o-*Chlorbenzaldehyde*-o-*nitrophenylhydrazone* (XIII).—A mixture of *o*-nitrophenylhydrazine (2 g.) and *o*-chlorbenzaldehyde (2 g.) in alcoholic solution was heated under reflux for about 20 minutes when an orange yellow precipitate gradually formed in the solution. The solution was allowed to cool and the precipitate filtered, washed with dilute hydrochloric acid and alcohol and finally crystallised from the same solvent in orange yellow plates. It is soluble in

acetone, acetic acid and chloroform, m.p. 171°. (Found: N, 15·23. $C_{13}H_{10}O_2N_8Cl$ requires N, 15·27 per cent.).

Reduction of the above Compound: Formation of 2:3:7:8-*Dibenzo*-1:4:5-*octatriazine* (XIX).—The above hydrazone (3 g.) was heated under reflux with granulated tin (10 g.) and concentrated hydrochloric acid (60 c.c.) for an hour when an orange coloured clear solution was obtained which, however, became colourless on further heating. After the removal of tin, the solution was evaporated almost to dryness on the water-bath when it gave a white shining crystalline residue which was crystallised from dilute hydrochloric acid, m. p. 285°. It is soluble in hot water and gives silver chloride with silver nitrate solution.

The free *base* was obtained as a white crystalline mass by adding ammonia to an aqueous solution of the hydrochloride and was crystallised from alcohol in shining colourless plates, m.p. 217-218°. It is insoluble in boiling water. (Found: N, 20·11. $C_{13}H_{11}N_3$ requires N 20·09 per cent.).

Glyoxal-o-nitrophenylosazone (XIV).—An aqueous solution of *o*-nitrophenylhydrazine hydrochloride (3 g.) and glyoxal sodium bisulphite (2·5 g.) was heated under reflux for about fifteen minutes when a red solid separated out. It was filtered, washed with hot water and was crystallised from acetic acid in red, minute needles. It is insoluble in water, hydrochloric acid and alcohol, m.p. 279-280° with decomposition. (Found: N, 25·49. $C_{14}H_{12}O_4N_6$ requires N, 25·6 per cent.).

Bis-benziminazole (XX).—3 Gm. of the compound (XIV) were reduced with tin and hydrochloric acid in the usual manner. Tin removed by sulphuretted hydrogen and the solution was then evaporated on the water-bath almost to dryness when a brownish white crystalline mass was obtained and was crystallised from alcohol, m.p. 253° with decomposition. It gives silver chloride with silver nitrate solution. (Found: N, 15·96; Cl, 20·18. $C_{14}H_{10}N_4$, 2HCl, $2H_2O$ requires N, 16·37; Cl, 20·46 per cent.).

The free *base* was obtained by adding ammonia to an aqueous solution of the above hydrochloride as a brown flocculent precipitate which was crystallised from alcohol, m.p. above 300°. (Found: N, 23·74. $C_{14}H_{10}N_4$ requires N, 23·93 per cent.).

The *diacetyl* derivative was prepared by heating the hydrochloride with acetic anhydride on a sand-bath under reflux for about 15 minutes. The clear solution thus obtained gave, on cooling, a

colourless crystalline product which was recrystallised from acetic acid in needles, m.p. 183-184°. (Found: N, 17·33. $C_{13}H_{14}O_2N_4$ requires N, 17·61 per cent.).

Methyl-o-nitrophenyl-dithiocarbazinate (XV).—Carbon disulphide (10 g.) and potassium hydroxide (5·5 g.) dissolved in the least quantity of water were added drop by drop to a solution of *o*-nitrophenylhydrazine (10 g.) in 80 c.c. of alcohol at 0° when a blue coloured clear solution was obtained. The solution was allowed to stand for a few minutes in the ice-bath and methyl iodide (13 g.) was then added to it in several instalments. The solution gradually turned red and soon deposited shining red crystals which were washed with ice cold water and alcohol (dilute) and crystallised from the same solvent as beautiful red needles, m.p. 113-114°. It is soluble in ether, carbon bisulphide, benzene and toluene. (Found: N, 17·50. $C_8H_9O_2N_3S_2$ requires N, 17·28 per cent.).

Reduction of (XV): *Formation of* 2:3-*Benzo*-6-*methylthiol*-1:4:5-*triazine* (XXI).—The methyl ester (4 g.) was heated under reflux with granulated tin (10 g.) and concentrated hydrochloric acid (50 c.c.). A pink coloured solution was obtained within an hour which, however, became colourless on further heating. After removing tin, the solution was evaporated almost to dryness on the water-bath and was cooled. The crystalline hydrochloride thus obtained gave the free *base* on treatment with ammonia which was crystallised from dilute alcohol, m.p. 199-200°. It is insoluble in water but readily soluble in pyridine and acetic acid. (Found: N, 23·08. $C_8H_9N_3S$ requires N, 23·46 per cent.).

Di-o-nitrophenyl-carbohydrazide (XVI).—A benzene solution of *o*-nitrophenylhydrazine (5 g.) and 7·5 g. of 20 per cent. solution of phosgene in toluene were heated under reflux on the water-bath for about fifteen minutes when a yellow precipitate came out. It was filtered, washed with benzene and the unreacted *o*-nitrophenylhydrazine hydrochloride was washed away with boiling water. The residual yellow mass was then crystallised from acetic acid in beautiful yellow needles, m.p. 260-261°. It is insoluble in benzene and toluene sparingly soluble in alcohol but readily soluble in methyl alcohol, acetic acid and acetone. (Found: N, 25·19. $C_{13}H_{10}O_5N_6$ requires N, 25·30 per cent.).

Reduction of Compound (XVI): *Formation of* 2:3:9:10-*Dibenzo*-6-*keto*-1:4:5:7:8-*decapentazine* (XXII).—Di-*o*-nitrophenylcarbohydrazide (5 g.) was heated with tin (10 g.) and concentrated hydro-

chloric acid (60 c.c.) on a water-bath under reflux until a clear colourless solution was obtained. After removing the tin, the solution was evaporated almost to dryness on the water-bath and cooled. The reddish brown crystalline mass thus obtained was crystallised from dilute hydrochloric acid in brownish white prisms melting at 251-252° with decomposition and producing a blue colouration. It gives a red colouration with ferric chloride solution and silver chloride with silver nitrate. (Found: N, 15·88; Cl, 24·27. $C_{18}H_{18}ON_6$, 3HCl, $4H_2O$ requires N, 16·09; Cl, 24·14 per cent.).

The free Base.—The liberation of the free base from the above hydrochloride was tried with ammonia, but it was found to be very unstable particularly in presence of air.

Ethylo-nitrophenyl-carbazinate (XVII).—A benzene solution of *o*-nitrophenylhydrazine (5 g.) and ethyl chlorocarbonate (3 g.) was heated under reflux for about ten minutes when a brownish white mass separated out. It was filtered, washed with benzene and boiled with water for removing the nitrophenylhydrazine hydrochloride. The residue was crystallised from alcohol, m.p. 185°. (Found: N, 18·42. $C_9H_{11}O_4N_3$ requires N, 18·67 per cent.).

Our thanks are due to Sir P. C. Rây and Professor J. C. Ghosh for the kind interest they have taken in this work.

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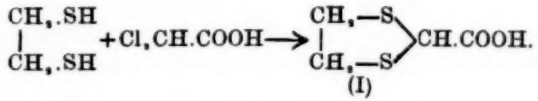
Organic Cyclic Polysulphides: Condensation of Ethylene Mercaptan with Di- and Tri-chloracetic Acids.

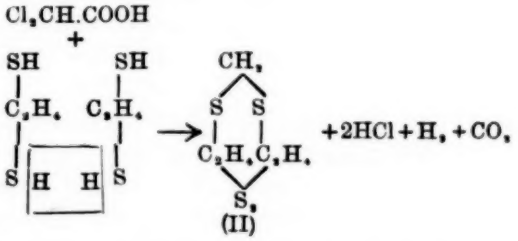
By Gopâl Chandra Chakravarti and Jogendra Mohan Saha.

The interesting physical and chemical properties possessed by triethylene tri- and tetra-sulphides (Rây, *J. Chem. Soc.*, 1920, **117**, 1090 ; 1922, **121**, 1207) and benzylidene diethylene tri- and tetra-sulphides (Rây, *J. Chem. Soc.*, 1924, **125**, 1141) led the present authors to undertake a more detailed investigation of a further series of cyclic polysulphides and their derivatives. It was anticipated that the reaction between dichloracetic acid and dithioethylene glycol would take the following course:—



(I)

resulting in the formation of the polysulphide (I). When, however, a mixture of equimolecular quantities of the acid and the mercaptan was heated either on the water-bath or gently boiled on the sand-bath, a compound with the composition, $C_5H_{10}S_4$, was isolated. The reaction can evidently be expressed in the following manner:—

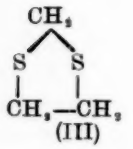


(II)

No reaction takes place if benzene is used as the solvent. But when dichloracetic acid and ethylene mercaptan are heated in xylene solution three isomeric compounds are obtained: one melting at 192-194°, another melting at 83-84° and the third, a liquid, all having the empirical formula $C_5H_8S_4$, which is the cyclic polysulphide (III).

It is extremely probable that the above compounds represent different polymerides of (III).

Ethyldichloracetate and potassium dithioethylene glycol gave rise to two different oily products which conform to the formulae (IV) and (V).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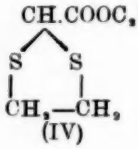
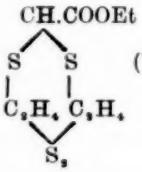

(IV)


(V)

The compound (V) was formed only in small quantities. Attempts were therefore made to convert compound (IV) successively into compounds (I) and (III) by the usual methods of hydrolysis and heating. But all attempts to obtain the latter failed owing probably to the difficulty in identifying the degradation products. The investigations of Rây (*loc. cit.*) and others (Fromm and Engler, *Ber.*, 1925, **58**, 1916, etc.,) show that many of the cyclic polysulphides can exist in several polymeric forms. The failure to identify the product of hydrolysis and heating of compound (IV) as any of the compounds (III) must be ascribed to the production of other polymers. Even the simplest compound ethylene disulphide has been obtained in four or five polymeric forms (*vide* Experimental). The expected compound (I) was however obtained by the interaction of potassium dichloracetate and potassium dithioethylene glycol in alcoholic solution.

Trichloracetic acid reacted with ethylene mercaptan under various conditions. No cyclic polysulphide containing the acid residue was formed in any of these reactions, the trichloracetic acid molecule only functioning as the oxidising agent by converting the mercaptan into various polymeric disulphides, except in one case only when a crystalline compound, m.p. 95-96° identical with the compound (II) was formed. The formation of this compound goes to show that trichloracetic acid is first reduced to dichloracetic acid which then reacts with the mercaptan to give rise to the compound (II) thus:

$$CCl_3.COOH + C_2H_4(SH)_2 = CHCl_2.COOH + C_2H_4S_2 + HCl.$$

Experimental.

Interaction of Ethylene Mercaptan and Dichloracetic Acid.—Six gm. of the mercaptan (2 mols.) and 9 gm. of the acid (1 mol.) were heated together either on a water-bath or gently boiled on a sand-bath for several hours. Copious evolution of hydrochloric acid, carbon dioxide and sulphuretted hydrogen gases took place. The dark violet coloured mass solidified on cooling and was well-washed with dilute caustic alkali and then with water. The alkaline wash water on acidification gave a very scanty green precipitate, but it was insufficient for purification and analysis. The brown residue was extracted three or four times with hot alcohol. The filtrate on concentration gave a crop of brownish needle-shaped crystals of pentamethylene tetra-sulphide (II) which were recrystallised from alcohol until they turned white, m.p. 96°. (Found: S, 65·8 ; C, 29·83 ; H, 4·52. $C_5H_{10}S_4$ requires, S, 64·6 ; C, 30·3 ; H, 5·1 per cent.). The residue was then successively and separately extracted with acetone, benzene and nitrobenzene. The products obtained by evaporating the solvents were found to be polymers of ethylene disulphide.

Interaction of Ethylene Mercaptan and Dichloracetic Acid in Xylene Solution.—Four gms. of the mercaptan (2 mols.) and 6 gm. of the acid (1 mol.) were heated together in 30 c.c. of xylene for about 29 hours. Evolution of HCl, CO_2 and H S gases took place. The solution was concentrated on the water-bath to about 10 c.c. and cooled. A granular crystalline precipitate was obtained. This was filtered, washed with cold alcohol and repeatedly crystallised from hot xylene. Fine yellow granular crystals of trimethylene disulphide (III), m.p. 192-194° soluble in benzene were obtained. (Found: C, 34·3 ; H, 6·4. $C_3H_6S_2$ requires C, 33·96 ; H, 5·6 per cent.).

The filtrate after the separation of the yellow substance was dissolved in benzene and well-washed with dilute caustic alkali and water. It was then filtered, dried with fused calcium chloride, again filtered and then evaporated. An oil mixed with a crystalline substance was obtained. The oil was extracted with a small quantity of ether leaving behind the white crystalline residue. After filtration the ether was driven out and the oil again extracted with a small quantity of ether. Finally on evaporation the ethereal solution gave

a slightly brown-coloured heavy oil with a sweet ordour. (Found: C, 34·2 ; H, 4·6 ; S, 61·38. $C_8H_6S_4$ requires C, 33·96 ; H, 5·6 ; S, 60·38 per cent.).

The white crystalline mass mentioned above was repeatedly crystallised from large amount of ether in which it is very sparingly soluble. White granular crystals, m.p. 83-84° were obtained. (Found: C, 33·51; H, 4·98. $C_8H_6S_4$ requires C, 33·96; H, 5·6 per cent.).

In the above reaction the yield of the yellow product was the largest whilst the other two were formed only in small quantities.

Interaction of Ethyl Dichloracetate and Monopotassium Ethylene Mercaptan.—Nine gm. of the potassium salt and 5·5 gm. of the ester and 50 c.c. of anhydrous alcohol were refluxed together for about 5 hours. The solution was filtered hot from the solid precipitate of potassium chloride, evaporated to dryness and the residue extracted with benzene. The benzene solution was first shaken up with dilute caustic alkali and then with water, filtered, dried, again filtered and the benzene removed. The oil thus obtained was repeatedly extracted with cold alcohol or ether. The residual oil was dissolved in benzene, filtered and evaporated to dryness when a brownish thick colourless oil was left behind. This is ethyl diethylene tetrasulphido acetate (V). (Found: S, 47·27 ; C, 34·35; H, 5·94. $C_8H_{14}O_2S_4$ requires S, 47·41; C 35·55; H, 5·19 per cent.).

The ethereal solution was evaporated to dryness and then extracted with a small quantity of ether leaving behind some insoluble oily and solid matters. The solution was evaporated and the previous process repeated several times until at last a transparent thick oil ethyl ethylene-disulphido acetate (IV), with a pleasant odour was obtained. (Found: C, 39·8; H, 5·89; S, 35·34. $C_6H_{10}O_2S_2$ requires C, 40·4; H, 5·6; S, 36·0 per cent.).

This oil was formed in larger amount in comparison with the previous one. It was dissolved in absolute alcohol and boiled with the calculated quantity of alcoholic potash for about two hours. The whole mass was evaporated to dryness and the residue dissolved in water and acidified with dilute hydrochloric acid. The turbid liquid was extracted with benzene and the benzene extract evaporated to dryness. The estimation of the percentage of sulphur in this acid shows that is most probably ethylene-disulphido-acetic

acid (*I*). Its properties correspond with those of the latter. (Found: S, 41·95. $C_4H_6O_2S_2$ requires S, 42·66 per cent.).

Interaction of Potassium Dichloracetate and Monopotassium Ethylene Mercaptan.—Potassium dichloracetate (4·25 g., potassium mercaptide (4·75 g.) and anhydrous alcohol (50 c.c.) were refluxed together for about an hour and filtered hot from the precipitate of potassium chloride. The filtrate was evaporated to dryness and the solid residue dissolved in water, filtered and acidified with concentrated HCl in the cold and the turbid solution extracted with benzene. The benzene solution was well washed with water, filtered, dried and again filtered and evaporated to dryness. The oil thus obtained was purified by a repetition of the processes of extraction with a small amount of ether, filtration and evaporation—every time leaving behind some brown amorphous residue. A heavy oil (I) of pungent odour insoluble in petroleum ether was obtained. It is strongly acid to litmus and decomposes alkaline carbonates and bicarbonates. (Found: C, 32·37; H, 4·7. $C_4H_6O_2S_2$ requires C, 32·00; H, 4·00 per cent.).

The oil-acid was neutralised by the required quantity of pure caustic potash solution, the solution was evaporated to dryness and the residue crystallised from alcohol. The *potassium salt* was obtained as a colourless mass. (Found: K, 19·63. $C_4H_5O_2S_2K$ requires K, 20·0 per cent.).

Interaction of Ethyl Trichloracetate and Ethylene Mercaptan.—The mercaptan (10 g.) and the ester (10 g.) were gently heated together for several hours on the sand-bath. Copious evolution of hydrochloric acid and sulphuretted hydrogen gases was noticed. The cold solid mass after washing with dilute alkali and water, was separated into different fractions by treatment with alcohol, chloroform, xylene and nitrobenzene. The products obtained from these solvents were amorphous and found to be polymerised ethylene disulphide. The ester was subsequently heated with the monopotassium salt of the mercaptan and also with its disodium salts in alcoholic and in benzene solutions—but only the polymers of ethylene disulphide were obtained. Next the monopotassium salt was shaken in the cold; ethylene disulphide was the only product.

Interaction of Trichloracetic Acid and Ethylene Mercaptan.—The mercaptan (10 g.), the acid (9 g.) and xylene (40 c.c.) were heated together for about 22 hours (benzene was first employed but no

reaction ensued even on continued boiling) on the sand-bath. Evolution of large quantities of hydrochloric acid, carbon dioxide and sulphuretted hydrogen gases took place. The solution was evaporated to dryness and well washed with dilute alkali and then with water. The alkaline filtrate on acidification yielded no precipitate. The residue was refluxed with alcohol, filtered and the solution concentrated. Fine needle-shaped crystals with a slight greenish tinge were obtained. These were purified by repeated crystallisation from alcohol. White needles, m.p. 95-96° identical with the compound (II) derived from dichloracetic acid and ethylene mercaptan were obtained (*vide supra*). The residue after extraction with alcohol was separated into three fractions by refluxing with benzene, xylene and nitrobenzene respectively, but the products obtained from these solutions were all amorphous compounds, indentical with the polymers of ethylene disulphide.

In conclusion, the authors take this opportunity of expressing their gratefulness to Sir P. C. Rây for his kind interest and help in this investigation.

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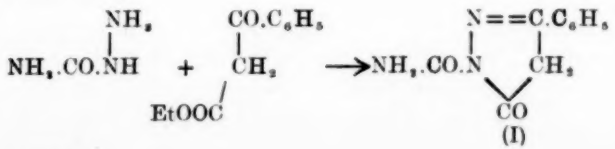
Synthesis in the Pyrazolone Series. Action of Thiosemicarbazide and Semicarbazide on Ketonic Esters. Part II.

By Satis Chandra De and Nirode Chandra Dutt.

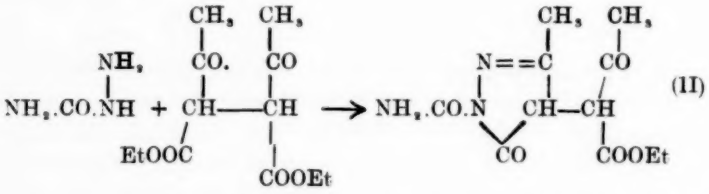
In a previous communication (This *Journal*, 1926, **3**, 30) it has been shown by one of us that thiosemicarbazide and semicarbazide can condense with acetoacetic ester to form pyrazolone derivatives, the reaction of course taking place in two distinct phases. In the first phase of the reaction a hydrazone is formed which in the second phase parts with a molecule of alcohol to yield the pyrazolone.

In the present paper our object is to study the behaviour of thiosemicarbazide and semicarbazide and their 4-substitution products on benzoylacetic ester and diacetosuccinic ester and to see whether it is possible to obtain pyrazolones from them also. As the result of our investigation it is found that the carbazides can be made to react with the ketonic esters to give pyrazolones. But one peculiarity to be noticed here is that while thiosemicarbazide gives with acetoacetic ester a hydrazone, such a compound could not be prepared by the authors from 4-substituted thiosemicarbazides and the ester. This is probably due to the fact that these substances show no tendency to react with the ketonic esters at the ordinary temperature but on heating the two components together in presence of alcohol they combine to yield pyrazolones, the intermediate hydrazones not being possible to isolate. Another interesting fact is that whereas acetoacetic ester combines with semi- and thiosemi-carbazides to form hydrazones, the benzoylacetic or diacetosuccinic ester shows no tendency to form such hydrazones with these components although the reaction proceeds at the ordinary temperature yielding the pyrazolone compounds. For example, benzoylacetic ester and semicarbazide give 3-phenylpyrazolone-1-carbamide (I) according to the following scheme:



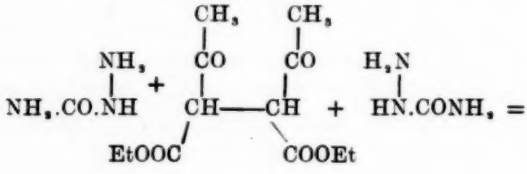
(I)

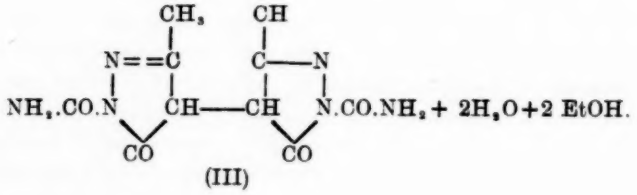
Similarly diacetosuccinic ester should react with semicarbazide in two different ways to yield pyrazolone derivatives with the elimination of water and alcohol. From one molecule of the ester and one of semicarbazide, a 3-methylpyrazolone-1-carbamide-4-acetoacetic ester (II) may result, thus:



(II)

This compound may then react with a second molecule of semicarbazide to give rise to a 4-bis-3-methylpyrazolone-1-carbamide (III), a compound which can also be derived from one molecule of the ester and two of semicarbazide. But by taking molecular proportions of the components a compound of formula (II) could not be prepared, the product always being the bis-pyrazolone. The reaction, therefore, proceeds according to the equation:





(III)

In the previous communication 3-methylpyrazolone-1-carbamide has been shown to be stable only in the cold as the carbamide group is very easily eliminated form this compound even by gentle warming with alcohol with the formation of 3-methylpyrazolone, a compound easily obtainable from acetoacetic ester and hydrazine hydrate. 3-Phenylpyrazolone 1-carbamide and 4-bis-3-methylpyrazolone-1-carbamide, on the contrary, are comparatively stable substances as

they do not part with the carbamide group even on prolonged boiling either with water or alcohol. 3-Phenylpyrazolone can, however, be obtained from 3-phenylpyrazolone -1 carbamide by heating the latter with alcoholic hydrochloric acid in a sealed tube. Bis-3-methylpyrazolone can be easily obtained from 4-bis-3-methylpyrazolone-1-carbamide by heating the latter at its melting point when it parts with the carbamide group.

It has also been shown that 3-methylpyrazolone-1-carbamide (or thiocarbamide) can react with a second molecule of acetoacetic ester to yield 3-methylpyrazolone-1-carbonyl-(or thiocarbonyl)-β-uramidocrotonic ester. But the pyrazolones derived from the interaction of benzoylacetic ester on semicarbazide and thiosemicarbazide as well as those derived from diacetosuccinic ester and the carbazides could not be made to react with a second molecule of acetoacetic or benzoylacetic ester.

Experimental.

Condensation of Benzoylacetic Ester with Thiosemicarbazide and its Substitution Products.

3-*Phenylpyrazolone*-1-*thiocarbamide*.—This compound was obtained when thiosemicarbazide hydrochloride and benzoylacetic ester were allowed to react in presence of sodium acetate: The ester (1 mol.) dissolved in alcohol was added to an aqueous solution of the hydrochloride of the base (1 mol.). After shaking the mixture for some time sodium acetate (1 mol.) was added and the mixture allowed to stand for two days. The solid crystalline product that separated out was filtered, washed with water, and crystallised from alcohol in white rectangles, m.p. 161°. (Found: N, 19·30. $C_{10}H_9ON_3S$ requires N, 19·18 per cent.).

The same compound was obtained much more easily by heating an alcoholic solution of benzoylacetic ester (1 mol.) with the carbazide hydrochloride (1 mol.) in the least quantity of aqueous sodium acetate solution. The pyrazolone so obtained is insoluble in ether, benzene and chloroform; slightly soluble in cold but easily so in hot alcohol.

4 : 4′-*Dibromo*-3-*phenylpyrazolone*-1-*thiocarbamide* was prepared by allowing an excess of bromine in acetic acid solution to react on 3-phenylpyrazolone-1-thiocarbamide suspended in the solvent. As

the reaction began with evolution of heat, the pyrazolone gradually went into solution and torrents of hydrobromic acid fumes were evolved. After stirring for some time a small quantity of the dibromoderivative separated as a red crytalline product. A further quantity was obtained by diluting the acetic acid solution with water. It was crystallised from dilute acetic acid in light orange-red microscopic crystals, which begin to shrink at 130° with the slow liberation of bromine. (Found: S, 8·83; Br, 42·65. $C_{10}H_7ON_3SBr_2$ requires S, 8·48; Br, 42·44 per cent.).

4-iso-*Nitroso*-3-*phenylpyrazolone*-1-*thiocarbamide*.—It was obtained by adding sodium nitrite solution to the pyrazolone suspended in acetic acid. The reaction began with the separation of a yellow crystalline product. This was collected, washed with water and crystallised from alcohol in yellow needles, m.p 174°. (Found: N, 22·70. $C_{01}H_5O_2N_4S$ requires N, 22·58 per cent.).

The *iso*nitroso compound has a strong acid reaction. It dissolves in alkali and from the alkaline solution it separates unchanged on acidification.

3-*Phenylpyrazolone*-1-*thiocarbophenylamide* was prepared from a mixture of equimolecular proportions of 4-phenylthiosemicarbazide and the ketonic ester in alcoholic solution. After heating for about three hours the solution was allowed to cool when the pyrazolone separated as white crystals, a further quantity being obtainable by adding water to the mother-liquor. The product crystallised from dilute alcohol in white long rectangles, m.p. 127°. (Found: N, 14·46. $C_{16}H_{13}ON_3S$ requires N, 14·24 per cent.).

3-*Phenylpyrazolone*-1-*thiocarbo*-p-*tolylamide*.—It was obtained from molecular proportions of 4-*p*-tolylthiosemicarbazide and the ketonic ester in alcoholic solution. On concentrating the solution and allowing it to stand with frequent scratching and shaking the pyrazolone was obtained as a white crystalline mass. This was filtered and then recrystallised from dilute alcohol in white rectangles, m.p. 106°. (Found: N, 13·77. $C_{17}H_{15}ON_3S$ requires N, 13·59 per cent.).

3-*Phenylpyrazolone*-1-*thiocarboethylamide*.—It was obtained by heating an alcoholic solution of 4-ethylthiosemicarbazide and the ester in molecular proportions. On allowing the cold solution to stand crystals gradually came out and after two days these were collected and crystallised from dilute alcohol in

white rectangles, m.p. 136°. (Found : N, 16·78. $C_{11}H_{13}ONS$ requires N, 17·00 per cent.).

Condensation of Benzoylacetic ester with Semicarbazide.

3-*Phenylpyrazolone*-1-*carbamide*.—This compound was prepared in the same way as the corresponding thio-compound by taking molecular proportions of the reactants. An aqueous solution of semicarbazide hydrochloride and sodium acetate was added to the ketonic ester diluted with alcohol and the mixture was vigorously shaken. After a short time a white crystalline precipitate was obtained. This was filtered, washed with water and crystallised from alcohol in white needles, m.p. 179°. (Found : N, 20·78. $C_{10}H_9O_2N_3$ requires N, 20·69 per cent.).

The same compound was also obtained by heating an alcoholic solution of the components. It is sparingly soluble in cold but easily so in hot alcohol ; insoluble in ether, benzene and chloroform. The carbamide group is not easily eliminated from this compound but on heating with alcoholic hydrochloric acid in a sealed tube at 120°-130° for several hours this group can be removed with difficulty and the hydrochloride of 3-phenylpyrazolone is formed from which by neutralisation with ammonia, the free base is obtained ; m.p. 236°, identical with the compound of Curtius (*J. pr. Chem.*, 1894, **50**, 515).

4 : 4'-*Dibromo*-3-*phenylpyrazolone*-1-*carbamide*.—It was obtained from an excess of bromine and the pyrazolone in acetic acid solution. During the addition of bromine great heat was evolved and hydrobromic acid fumes were produced. After some time the dibromo compound separated from the solution. This was filtered and crystallised from acetic acid ; m.p. 144°. (Found : Br, 44·20. $C_{10}H_7O_2N_3Br_2$ requires Br 44·32 per cent.).

4-iso*Nitroso*-3-*phenylpyrazolone*-1-*carbamide*.—It was prepared from the solution of the pyrazolone in acetic acid to which an aqueous solution of sodium nitrite was slowly added. The *iso*nitroso compound separated at once as yellow crystals. This was filtered, washed with water and recrystallised from alcohol ; m. p. 204°. (Found : N, 24·29. $C_{10}H_8O_3N_4$ requires N, 24·13 per cent.),

Condensation of Diacetosuccinic ester with Semicarbazide : Formation of 4-Bis-3-methylpyrazolone-1-carbamide :

To a solution of the ester (1 mol.) in alcohol was added a solution of semicarbazide hydrochloride (2 mols) in aqueous sodium acetate solution. The reaction began with evolution of heat and separation of the pyrazolone crystals. The mixture was then heated on the water-bath for 10-15 minutes to bring the reaction to an end. The crystals were filtered from the solution, washed with water and re-crystallised from alcohol ; m.p. 128°. (Found : N, 30·15. $C_{10}H_{12}O_4N_6$ requires N, 30·00 per cent.).

At its melting point it is at once converted into bis-3-methylpyrazolone with the elimination of the carbamide groups. The pyrazolone so obtained after crystallisation from water begins to turn brown at 255° and melts at 290°. (Found : N, 28·34. $C_8H_{10}O_2N_4$ requires N, 28·86 per cent.).

Condensation of Diacetosuccinic Ester with Thiosemicarbazides.

4-Bis-3-methylpyrazolone-1-thiocarbamide.—It was prepared from thiosemicarbazide (1 mol.) and the ester (1 mol.) using alcohol as solvent. After heating for some time a clear solution was obtained. The filtrate on cooling was filled with crystals. This was re-crystallised from alcohol in white rectangles, m.p. 197°. (Found: N, 27·15. $C_{10}H_{12}O_2N_6S_2$ requires N, 26·92 per cent.).

4-Bis-3-methylpyrazolone-1-thiocarbophenylamide.

It was obtained as before from 4-phenylthiosemicarbazide (2 mols.) and the ester (1 mol.). This was crystallised from alcohol in white long rectangles, m.p. 191°. (Found : N, 18·22. $C_{22}H_{20}O_2N_6S_2$ requires N, 18·10 per cent.).

4-Bis-3-methylpyrazolone-1-thiocarbo-p-tolylamide.—It was obtained from 4-*p*-tolylthiosemicarbzide (2 mols.) and the ester (1 mol.). The pyrazolone was recrystallised from alcohol in white needles, m.p. 201°-202°. (Found: N, 17·25. $C_{24}H_{24}O_2N_6S_2$ requires N, 17·07 per cent.).

4-Bis-3-methylpyrazolone-1-thiocarboethylamide.—It was obtained from 4-ethlylthiosemicarbazide (2 mols.) and the ester (1 mol.) in alcoholic solution. The pyrazolone separated from the solution on long standing in white rectangles, m.p. 191°. (Found : N, 22·98. $C_{14}H_{20}O_2N_6S_2$ requires N, 22·82 per cent.).

Condensation of Acetoacetic Ester with Substituted Thiosemicarbazides.

3-*Methylpyrazolone*-1-*thicarbophenylamide*.—It was obtained from 4-phenylthiosemicarbazide and acetoacetic ester in alcoholic solution. The mixture was heated for about two hours and the solution allowed to cool when crystals separated out. This was recrystallised from alcohol in white rectangles, m.p. 117°. (Found : N, 18·20. $C_{11}H_{11}ON_3S$ requires N, 18·02 per cent.).

3-*Methylpyrazolone*-1-*thiocarbo*-p-*tolylamide* was prepared by heating an alcoholic solution of 4-*p*-tolylthiosemicarbazide and the ketonic ester. The compound separated on long standing. This was crystallised from dilute alcohol in white rectangles, m.p. 121°. (Found : N, 17·21. $C_{12}H_{13}ON_3S$ requires N, 17·00 per cent.).

3-*Methylpyrazolone*-1-*thiocarbomethylamide*.—By heating for about for two hours an alcoholic solution of 4-methylthiosemicarbazide and the ketonic ester and concentrating the solution and allowing to stand crystals made their appearance after two days. This was crystallised from dilute alcohol ; m.p. 84°. (Found : N, 24·75. $C_6H_9ON_3S$ requires N, 24·56 per cent.).

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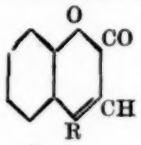
Formation of Heterocyclic Compounds. Part III. Interaction of *cyclo*Hexanone-2-carboxylates with Phenols.

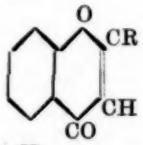
By Hemendra Kumar Sen and Umaprasanna Basu.

The condensation between β-ketonic esters and phenols formed the subject of extensive investigation for the syntheses of benzopyrone derivatives by numerous workers (Pechmann, *Ber.*, 1844, **17**, 929, 1646, 2187 ; 1839, **32**, 3681 ; 1901, **34**, 423 ; Biginelli, *Gazzetta*, 1895, **24**, *ii*, 492 ; Pechmann, *Ber.*, 1901, **34**, 38 ; Simonis and Petschek, *Ber.*, 1913, **46**, 2014 ; Simonis and Lechmann, *Ber.*, 1914, **47**, 697 ; Simonis and Remmert, *ibid*, p. 2229; see also Heilborn, Barnes and Morton, *J. Chem. Soc.*, 1923, **123**, 2569). Substituted acetoacetic esters like CH_3 CO. CH (R). CO_2 Et (R=benzyl, phenyl, benzoyl), ethyl α-benzoyl-β-phenyl propionate and ethyl α-phenyl formylacetate (Jacobson and Ghosh, *J. Chem. Soc.*, 1915, **107**, 424, 959, 1051), ethyl β-keto-γ-phenyl butyrate (Baker and Robinson, *J. Chem. Soc.*, 1925, **127**, 1984), acetone dicarboxylic acid (Dey, *J. Chem. Soc.*, 1915, **107** 1606) and similar other β-ketonic esters also condense readily with phenols in presence of concentrated sulphuric acid, hydrogen chloride, and zinc chloride to give rise to α-pyrone derivatives.

As is well-known there are two possibilities in the mechanism of the reaction between a β-ketonic ester and phenol, one giving rise to a benzo-α-pyrone derivative (coumarin) as in (I) and the other to a benzo-γ-pyrone derivative (chromone) as in (II):



I



II

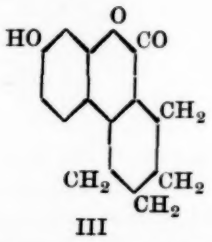
On consulting the literature on the subject it was found that the usual course of reaction is according to (I), *i.e.*, in ordinary instances using sulphuric acid, hydrochloric acid, or zinc chloride, β-ketonic esters give rise to benzo-α-pyrone derivatives. But using a condensing agent like phosphorous pentoxide, Simonis and his collaborators, however, (*loc. cit.*) prepared benzo-γ-pyrone derivatives from methyl

and ethyl derivatives of acetoacetic ester and phenols. The issue, therefore, is whether these reactions depend to a large extent on the reactivity of the methylene hydrogen atoms in the β-ketonic ester or on the condensing agent used. It is now generally admitted (see Baker and Robinson, *loc. cit.*) that the usual course of reaction is according to (1) and the benzo-γ-pyrone derivatives result only when the condensing agent is very strong such as phosphorus pentoxide.

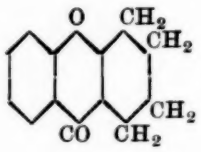
It appeared to be of importance to ascertain whether a cyclic β-ketonic ester such as ethyl *cyclo*hexanone 2-carboxylate in which the reactive methine group is situated in the nucleus has any influence in changing the course of such reactions.

After the work was continued for some time, it was noted that Dieckmann (*Annalen*, 1901, **317**, 27), while describing the condensation of ethyl *cyclo*hexanone-carboxylate and ethyl *cyclo*pentanone-carboxylate with resorcinol, assumed that in such condensation α-pyrone derivatives are produced. As the influence of the reduced benzene ring of hydroxymethylene *cyclo*hexanone (Sen-Gupta, *J. Chem. Soc.*, 1915, **107**, 1347) and *cyclo*hexanone-carboxylate (Sen and Bose, *J. Indian Chem. Soc.*, 1927, **4**, 51) was being studied at this time, a repetition of Dieckmann's results was considered necessary, specially in view of certain interesting criticisms put forward by Baker (*J. Chem. Soc.*, 1925, **127**, 2349) in connection with the γ-pyrone constitution of compounds described by Jacobson and Ghosh (*loc. cit.*).

Ethyl *cyclo*hexanone-2-carboxylate may be regarded as a substituted β-ketonic ester and as such, if the explanation of Jacobson and Ghosh, that with the heavier substitution of the methylene hydrogen the chance of γ-pyrone formation increases, be taken as correct, then the products described in this investigation should be in all probability γ-pyrone derivatives, although both α-and γ-pyrone structures are possible:—



III



IV

It has been proved, however, that a ketonitrile of the type —CO—$\dot{\underset{\bullet}{C}}$—CN condensing with a phenol gives rise to imino

compounds which on subsequent hydrolysis yields α-pyrones (Sonn, *Ber.*, 1918, **51**, 821, 1829; Bargellini and Forti-Forli, *Gazzetta*, 1911, **41**, *i*, 747 ; Baker, *loc. cit.*). Accordingly 2-cyano-*cyclo*hexanone was condensed with resorcinol ; the product obtained on hydrolysis of the intermediate compound was found to be identical with that obtained from ethyl *cyclo*hexanone carboxylate and resorcinol. The identity of the two products was further established by preparing acetyl derivatives and comparing their properties. This would indicate that the products described below are α-pyrone and not γ-pyrone derivatives. The influence of condensing reagents in changing the course of reaction (*loc. c.*) was next studied.

Accordingly attempt was made to produce the corresponding γ-pyrone derivatives by the use of phosphorus pentoxide but no product could be isolated.

However likely the α-pyrone constitution might thus appear to be, the behaviour with alkali of the *m*-cresol and α-naphthol condensation products with the ethyl *cyclo*hexanone carboxylate was somewhat peculiar. As α-pyrones, they were expected to dissolve in warm or boiling alkali, even though their ultimate decomposition may be difficult. The resorcinol derivative naturally dissolved readily in alkali by virtue of the one hydroxyl group present in it ; but when this hydroxyl group is acetylated benzoylated or alkylated, the resulting product no longer dissolves in alkali. Moreover, the condensation product with resorcinol, even on prolonged ***boiling with concentrated alkali***, does not undergo any fission and can be recovered unchanged on acidification. It would appear from the reasonings above that in all probability the condensed ring form of the products inhibits dissolution in alkali—a fact which should not be at the present stage regarded as indicative of a γ-pyrone structure. On fusion, however, of the resorcinol derivative with *caustic potash* at 190°-200° for a few minutes, two products were isolated, one melting at 230° (the parent substance had m.p. 202°) and the other at 120° which was identified as benzoic acid. The product melting at 230° has not been definitely identified yet, but it is in all probability a dehydrogenated coumarin derivative.

The attendant formation of benzoic acid may be regarded as a proof of the dehydrogenation of the *cyclo*hexane ring, as it is hardly to be expected that the benzoic acid should be derived from the resorcinol part of the compound. The usual experience under

such circumstances is to meet with resorcylic acid or resorcinol. In the present case also some resorcinol would be expected, which, however, could not be isolated probably on account of its low yield. Further investigation is in progress.

Experimental.

1. *Condensation of Ethyl* cyclo*Hexanone-2-carboxylate with Resorcinol: Formation of* 3:4-*Tetrahydrobenzo-7-hydroxy-coumarin* (III).

Ethyl *cyclo*hexanone-2-carboxylate was prepared according to Kötz's method (*Annalen*, 1925, **342**, 346) and obtained as a colourless liquid, b.p. 104-107°/10 mm. The yield was about 65 per cent. of the weight of *cyclo*hexanone used.

To a well cooled intimate mixture of resorcinol (2·5 g.) and ethyl *cyclo*hexanone-2-carboxylate (4 g.), well cooled strong sulphuric acid (20 c.c.) was gradually added with vigorous shaking. Within an hour a clear deep red solution having a violet fluorescence was obtained. The flask, being corked, was left overnight in an ice-chamber. Next day, the solution was poured over powdered ice when a pasty substance separated. This was purified by dissolving in dilute caustic soda solution and precipitating with dilute sulphuric acid. It crystallises from dilute alcohol in fine needles, melting at 201-202°.

To obtain a purer product in good yield the ester (2 g.) was intimately mixed with resorcinol (1·2 g.) and the mixture was slowly treated with concentrated sulphuric acid (6 c.c.) allowing the temperature to rise. The flask was shaken after each addition. After two hours the deep red solution was poured over powdered ice when a pasty mass was obtained. On adding a few c.c. of rectified spirit and stirring the mass, a solid separated. This was filtered, washed and dried. Crystallising from rectified spirit with the addition of a few drops of water, it melts at 202°. The yield is almost theoretical. (Found: C, 72·16; H, 5·69. $C_{13}H_{12}O_3$ requires C, 72·22; H, 5·55 per cent.).

This condensation product (which was described by Dieckmann as 1:2-*cyclo*tetramethylene umbelliferone melting at 203-204°) readily dissolves in dilute alkali or alkali carbonate to a yellow solution from which it is reprecipitated unchanged by acid. Concentrated sulphuric acid dissolves it with a violet fluorescence; from the acid solution the product can be recovered on dilution

with water. Ferric chloride imparts no coloration to its alcoholic solution.

Attempt to condense by Phosphorus Pentoxide.—Resorcinol (5 g.), *cyclo*hexanone carboxylate (5 g.) and phosphorus pentoxide (8 g.) were heated on a water-bath for half an hour and then over a sand-bath for a few minutes. It was then treated with resorcinol (5 g.) and the oxide (7 g.) and again heated on a water-bath for about 3 hours. On adding water to the product and on subsequent usual treatment, no condensation product was obtained; only a tarry matter separated out.

Next a mixture of resorcinol (2·5 g.), the ester (4 g.) and the oxide (16 g.) was taken in xylene (about 60 c.c.) and heated under reflux on a sand-bath for 4 hours. In this case nothing but a resinous product separated out after subsequent treatment of the reacted mass.

Action of Alkali on 3:4-Tetrahydrobenzo-7-hydroxycoumarin.—The coumarin derivative (3 g.) was dissolved in potassium hydroxide (20 g. in 20 c.c. water) and heated under reflux on a sand-bath for about 5 hours. The solution was found to contain an oily liquid which was extracted with ether. The ethereal solution was taken, ether evaporated off when a faint yellow coloured liquid (about 0·5 c.c.) having an odour like that of *cyclo*hexanone was obtained. On treatment with sodium acetate and semicarbazide hydrochloride a solid product was obtained with much difficulty. On crystallisation from dilute rectified spirit it melted at 175-176° sintering at 160°. The mixed m.p. of this substance with the semicarbazone of *cyclo*hexanone (m.p. 170°) was 142-143°.

The alkaline solution on acidification with dilute sulphuric acid gave a solid product which was dissolved in caustic soda solution and treated with carbon dioxide. The solid separated was found to be the original substance. The filtrate was again acidified with dilute sulphuric acid and shaken up with ether. The ethereal solution on evaporation gave a minute quantity of an oily product which on scratching turned into a pasty magma-like substance. Thus it was found that the major portion of the substance remained unchanged.

Next the coumarin derivative (3 g.) was fused with solid caustic potash (15 g.) at 190-200° for about ten minutes. The fused mass was dissolved in water and filtered. The dark coloured filtrate on acidification with hydrochloric acid gave a product (about 0·8 g.) which on crystallisation from dilute alcohol melts

at 230°. It is probably a dehydrogenated coumarin derivative. (Found: C, 73·23; H, 4·12. This corresponds to the empirical formula $C_{13}H_8O_3$ which requires C, 75·58; H, 3·77 per cent.).

The substance dissolves like the parent compound, in alkali and alkali carbonate with a yellow coloration. It gives a light green fluorescence with concentrated sulphuric acid. Ferric chloride solution gives no coloration. The *benzoyl* derivative prepared in pyridine solution melts at 195°. It is insoluble in alkali or alkaline carbonate, but concentrated sulphuric acid gives a grass-green fluorescence.

The filtrate, after acidification with hydrochloric acid and extraction with ether, gives a viscous mass from which benzoic acid can be isolated by extraction with petroleum ether.

Acetyl Derivative of the above Coumarin Derivative.—The substance (1·4 g.) was heated with acetic anhydride (0·3 g.) and fused sodium acetate (1 g.) under reflux on a sand-bath for one hour. The solution was then poured over water when a solid separated (yield, 90 per cent.). On crystallising from alcohol it melted at 186-187°. (Found: C, 70·23; H, 5·58. $C_{15}H_{14}O_4$ requires C, 69·77; H, 5·43 per cent.).

Methyl Ether.—This was prepared by treating the alkaline solution of the substance with excess of dimethyl sulphate. It crystallises from dilute alcohol in fine needle-like crystals melting at 121-122°. (Found: C, 72·83; H, 6·1. $C_{14}H_{14}O_3$ requires C, 73·04; H, 6·09 per cent.).

Benzoyl Derivative.—The substance (0·5 g.) was dissolved in pyridine and treated with a few drops of benzoyl chloride; a solid separated. The tube was warmed and water was added, when an oil was obtained. On allowing the oil to cool and scratching with a rod, a solid separated out which on crystallisation from rectified spirit melted at 157° sintering a few degrees earlier. (Found: C, 74·84; H, 5·19. $C_{30}H_{16}O_4$ requires C, 75·0; H, 5·0 per cent.). All these derivatives are insoluble in alkali or alkaline carbonate.

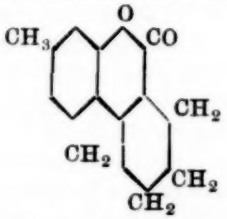
*Condensation of 2-Cyano*cyclo*hexanone with Resorcinol.*—2-Cyano-*cyclo*hexanone was prepared from 2-hydroxymethylene *cyclo*hexanone and hydroxylamine hydrochloride according to the method of Auwers, Bahr and Frese (*Annalen*, 1925, **441**, 43, 68) and obtained as a colorless liquid, b. p. 149-150°/25 mm. (yield, 29 per cent.).

Concentrated sulphuric acid (30 c.c.) was slowly added to a mixture of cyano-*cyclo*hexanone and resorcinol without allowing the

temperature to rise. After 36 hours the reaction product was poured over powdered ice, when a yellow solid (3 g.) was obtained after a few hours. This nitrogen containing compound was insoluble in alcohol, acetic acid water, and in most ordinary organic solvents, but was soluble in conc. sulphuric acid and alkali. It melted at 290°. The substance (2 g.) was heated with a 15 per cent. solution of caustic potash (25 c.c.) under reflux for 3½ hours when a strong smell of ammonia was perceived. The dark liquid formed, on dilution with water and on acidification with hydrochloric acid, yielded a solid product which on crystallising from dilute alcohol melted at 198°. The mixed melting point of this compound with that obtained from ethyl *cyclo*hexanone-2-carboxylate and resorcinol (m.p. 202°) was 201°.

The above compound was acetylated by heating under reflux for an hour with acetic anhydride and fused potassium acetate. The product obtained on crystallisation from alcohol, separated in needles, m. p. 184-185°. The mixed melting point of this derivative with the acetyl derivative described above (*loc. cit.*) is 186-187°. Thus the two products, one obtained from ethyl *cyclo*hexanone-2-carboxylate and resorcinol, and the other from 2-cyano-*cyclo*hexanone and resorcinol, are identical.

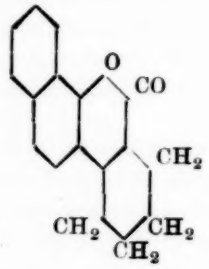
Condensation of Ethyl cyclo*Hexanone-2-carboxylate and* m-*Cresol: Formation of* 3:4-*Tetrahydrobenzo-7-methylcoumarin.*



Concentrated sulphuric acid (25 c.c) was gradually added to an intimate mixture of *m*-cresol (4 g.) and the ester (6.5 g.) with shaking and without allowing the temperature to rise. A dark red solution was soon obtained. Next morning the solution was poured over ice water when an oil separated, which on treatment with alcohol turned into a solid mass (about 4 g.; yield, 50 per cent.). It crystallised from diluted rectified spirit in long needles melting at 119°. (Found: C, 78·57; H, 6·49. $C_{14}H_{14}O_2$ requires C, 78·50; H, 5·54 per cent.).

This coumarin derivative is insoluble even in a strong caustic soda solution. On boiling the solution the substance melts, and forms an oil which again solidifies on cooling. It is soluble in strong sulphuric acid without any coloration or fluorescence; from this acid solution it can be recovered unchanged on dilution with water.

Condensation of α-Naphthol with cyclo*Hexanone-2-carboxylate*: *Formation of* 3:4-*Tetrahydrobenzonaphthocoumarin*:

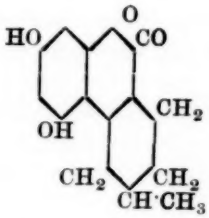


α-Naphthol (3·2 g.) was dissolved in the ester (4·2 g.) and the solution was slowly treated with concentrated sulphuric acid (6 c.c.). The mixture became warm and a deep red solution was obtained. Next morning it was found that a certain amount of solid had separated out. The contents of the flask were poured over powdered ice and the solid formed collected (6 g., yield, theoretical). In another preparation it was found that it is unnecessary to keep the reaction mixture over-night. The reaction product was found to be usual after pouring the liquid over powdered ice even after 2 hours. Crystallising from alcohol it melted at 190°. (Found: C, 82·52; H, 5·86. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6 per cent.).

This coumarin derivative gives no coloration with ferric chloride, is insoluble in alkali but soluble in concentrated sulphuric acid with yellow coloration and a sea-green fluorescence.

Nitro Derivative.—To concentrated sulphuric acid (1 c.c.), strong nitric acid (1 c.c.) was carefully added, and to the mixture a solution of the above compound (1 g.) in glacial acetic acid was added. After the reaction had subsided, the flask was cooled and the contents poured over powdered ice when a yellow substance separated. Crystallising from glacial acetic acid thrice, it melted at 244°, sintering a few degrees earlier. (Found: N, 5·01. $C_{17}H_{13}O_4N$ requires N, 4·75 per cent.).

*Condensation of Phloroglucinol and Ethyl 5-Methyl-cyclo**Hexanone-2-carboxylate*: *Formation of* 3: 4-*Tetrahydro-4'-methyl-benzo-5:7-dihydroxycoumarin.*

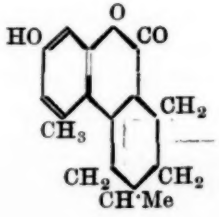


The ester was prepared in the usual way from *m*-methyl-*cyclo*hexanone which yields about 61 per cent. of its weight of 5-methyl-*cyclo*hexanone-2-carboxylate as a colorless liquid, b.p. 136-140°/25 mm.

The ester (6 g.) and phloroglucinol (4 g.) were mixed with glacial acetic acid (4 c.c.) and finely powdered fused zinc chloride (27 g.) was added. The mixture was heated at about 115° for 5 hours with continuous stirring when it turned into a viscous mass. Next morning it was boiled with water when a yellow granular substance (about 6 g.) was obtained (yield, 75 to 80 per cent.). It was difficult to crystallise it. The substance was dissolved in ether and petroleum ether was then added when a product was obtained. This was again dissolved in ether and treated with animal charcoal. From the filtrate on spontaneous evaporation, a white solid was obtained, melting at 264-66°, sintering a few degrees earlier. (Found: C, 68·0; H, 5·49. $C_{14}H_{14}O_4$ requires C, 68·29; H, 5·69 per cent.).

It is easily soluble in warm alkali, and in concentrated sulphuric acid with yellow coloration but with no fluorescence. Ferric chloride imparts no coloration to its alcoholic solution.

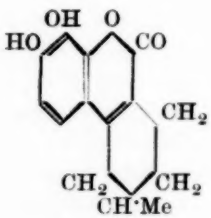
*Condensation of Orcinol and 5-Methyl-*cyclo*hexanone-2-carboxylate*: *Formation of* 3:4-*Tetrahydro-4'-methylbenzo-5-methyl-7-hydroxycoumarin.*



To an intimate mixture of the ester (3 g.), and orcinol (2 g.), concentrated sulphuric acid (10 c.c.) was gradually added with shaking and without allowing the temperature to rise. Soon a clear red solution was obtained. It was left overnight. Next day the red solution was poured over ice when a pasty mass separated. On adding rectified spirit a substance (3 g.) was obtained in granular form (yield, 75 per cent.). Crystallising from rectified spirit diluted with a few drops of water it was obtained in fine needles, m.p. 249°. (Found: C, 73·53 ; H, 6·81. $C_{18}H_{16}O_3$ requires C, 73·77 ; H, 6·56 per cent.).

It is soluble in caustic soda solution with yellow coloration but imparts no coloration to alcoholic ferric chloride. Concentrated sulphuric acid dissolves it with a yellow coloration.

Condensation of Pyrogallol with 5-Methyl-cyclohexanone-2-carboxylate : Formation of 3 : 4-Tetrahydro-4'-methylbenzo-7 : 8-dihydroxycoumarin.



A mixture of pyrogallol (2·5 g.) and the ester (3·7 g.) was treated with concentrated sulphuric acid (10 c.c.) in the usual way. Next morning the deep red solution obtained, was poured over powdered ice when a grey coloured substance (4·8 g.) was obtained. It crystallises from methyl alcohol in needles, m.p. 231°. (Found: C, 68·1 ; H, 5·89. $C_{14}H_{14}O_4$ requires C, 68·29 ; H, 5·69 per cent.).

The condensation product readily dissolves in alkali from which it may be reprecipitated unchanged by the addition of acid. Concentrated sulphuric acid dissolves it with yellow coloration and emerald green fluorescence ; from the acid solution it may be recovered on dilution with water. Ferric chloride imparts no coloration to its alcoholic solution.

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The Alkaloids of Kurchee Bark (*Holarrhena Antidysenterica*). Part I.

A Preliminary Note on Two New Alkaloids discovered in Indian *Holarrhena*.

By Sudhamoy Ghosh and Nagendra Nath Ghosh.

A large volume of chemical work has been done on the alkaloids of *Holarrhena* both in Europe and in India. The present work was undertaken with a view to study the pharmacological action of the alkaloids present in Indian *Holarrhena*. The recent work of Chopra and Ghosh (*Indian Medical Gazette*, 1927, **62**, 132,) on the pharmacological action of conessin has aroused wide interest in the alkaloids of *Kurchee* as a good drug. It was thought desirable to make a systematic study of the action of the individual alkaloids in *Kurchee* and also to see if the total alkaloids could be utilised and the product made into an article of commerce.

As a result of this investigation, two new alkaloids have been isolated in addition to conessine already known to be present in the bark of *Holarrhena antidysenterica*. The present paper records only the detailed method of their isolation and also some decisive evidences as to their being quite new alkaloids. Further work on these alkaloids is in progress and the full analytical data will be communicated later.

Ulrici (*Archiv. Pharm.*, 1918, **256**, 57) worked on the bark of *Holarrhena africana* and described in detail the isolation of the different alkaloids in it. He found the following alkaloids: (1) Conessin, $C_{23}H_{38}N_2$, large cubical crystals (unstable), m.p. 125°; also needles m.p. 121·5°; (2) a base $C_{24}H_{40}N_2$ of m.p. 121·5° and (3) homoconessin (dimethylconessin $C_{25}H_{42}N_2$) broad needles, m.p. not given. Giemsa and Halberkann (*Archiv. Pharm.*, 1918, **256**, 201), however, working on the same bark isolated only conessin $C_{24}H_{40}N_2$, which crystallises in flat needles or tablets, melting at 123°-124°. The homo-conessin of Ulrici was found by them to be identical with conessin.

Pyman (*J. Chem. Soc.*, 1919, **115**, 163), who worked on the alkaloids of *Holarrhena congolensis*, Stapf., found the following: (1) Conessine, $C_{24}H_{40}N_2$, large colourless plates, m.p. 125° and (2) holarrhenine, $C_{24}H_{38}ON_2$, silky needles, m.p. 197°–198°; $[\alpha]_D = -7{\cdot}1°$ (in $CHCl_3$); $[\alpha]_D$ of $C_{24}H_{38}ON_2$. $2HBr = +12{\cdot}1°$.

Kanga, Ayyar and Simonsen (*J. Chem. Soc.*, 1926, **129**, 2123) working on the seeds of Indian *Kurchee* (*Holarrhena antidysenterica*) isolated only pure conessine, $C_{24}H_{40}N_2$, m.p. 120°-121° (125° when crystallised from acetone) and studied some of its decomposition products.

Recently, Caius and Mhaskar (*Indian Medical Research Memoir*, No. 6, May, 1927) made a detailed study of both the seeds and bark of Indian *Kurchee*. They found only 0·025% of alkaloid in the seeds and 0·022% in the bark. They have isolated and purified only conessine and described in detail some of the colour reactions and tests of this alkaliod already studied carefully by Pyman. No mention is however, found in the published literature about the isolation of any other alkaloid in Indian *Holarrhena*.

Experimental.

A preliminary *assay* for the total alkaloids was made as follows: 20 gm. of the finely powdered bark (60 mesh) were treated with 10 c.c. ammonia (1:5) and then with 400 c.c. of a mixture of ether and chloroform. The mixture was agitated for 3 hours, 20 c.c. of water were added to it, agitated again and then allowed to settle. 200 C.c. of the clear, supernatant liquid (representing 10 g. of the bark) were filtered off into a separating funnel and shaken up repeatedly with dilute sulphuric acid till the whole of the alkaloid passed into the acid. The acid extract was filtered, made alkaline with ammonia and again taken up with chlorofrom. The chloroform solution was washed, transferred to a weighed vessel, the solvent carefully removed and the substance dried to a constant weight. The yield of total alkaloid was 1·28% of the weight of the dry bark. Exhaustion of the powdered bark with 95% alcohol in a Soxhlet, extraction of the residue with dilute acid and taking up the alkaloid with chloroform after adding excess of alkali gave nearly the same quantity of total alkaloids.

Preparation of total Alkaloids.—For complete examination, about two maunds (164 lbs.) of the powdered bark were percolated in the cold with rectified spirit till nearly exhausted. The major portion of the alcohol was distilled off and the remainder was then removed in partial vacuum. Two maunds of the bark thus gave 11 lbs. 6 oz. of the dark green, soft extract. It was repeatedly extracted with dilute hydrochloric acid until the last portion of the acid solution was nearly free from alkaloids. The acid solution was then carefully neutralised with dilute caustic soda and filtered. The filtrate was shaken with ether which removed some resinous, non-alkaloidal impurities. The aqueous liquid was then treated with slight excess of NaOH under constant stirring and the liquid kept cool by ice. The granular precipitate of the alkaloid was filtered and washed until free from excess of alkali. It was dissolved in dilute hydrochloric acid, made alkaline with caustic soda and shaken repeatedly with $CHCl_3$. The chloroform extract was washed, dried with anhydrous potassium carbonate, filtered and distilled. The residue was dried in vacuum over sulphuric acid. The quantity of alkaloid thus obtained was about 10% of the weight of the extract and about 0·7% of the weight of the bark. The large scale extraction with alcohol was done in a factory and the yield was, therefore, much less than what we obtained in our laboratory.

Separation and Purification of the Alkaloids.—The separation of the alkaloids is based on the principle that the tartrates of kurchicine and conessine are very slightly soluble in 95% alcohol, whereas the tartrate of the low-melting alkaloid kurchine, is freely soluble in it. Again the sulphate of kurchicine is practically insoluble in cold water whereas the sulphate of conessine is more soluble in it. Kurchicine is practically insoluble in petroleum ether whereas conessine is fairly soluble. The low-melting alkaloid is freely soluble in petroleum ether.

The total alkaloid was dissolved in 95% alcohol (4 to 6 times the weight of alkaloid taken) and to it was carefully added a saturated solution of tartaric acid in absolute alcohol until neutralised. The white, amorphous precipitate (A) obtained was filtered off and washed several times with 95 % alcohol. It was then dissolved in the smallest amount of boiling water, the solution treated with animal charcoal, filtered, and reprecipitated by adding excess of absolute alcohol. The tartrate was thus obtained as a white, amorphous powder. It was dissolved in water, the alkaloid liberated by NaOH

and taken up with $CHCl_3$. The $CHCl_3$ solution was washed, dried with K_2CO_3 and concentrated to a small bulk. A slight excess of petroleum ether was added when crystals began to appear. After several hours, the crystals (tufts of needles) were separated from the mother-liquor and washed with petroleum ether. They were redissolved in the smallest amount of $CHCl_3$ and crystallised again by addition of petroleum ether. The substance began to melt at 173° and it was complete at 175°. The amount of this new alkaloid (designated "kurchicine") was about 0·12% of the weight of the bark.

The substance was further purified by dissolving in hot dilute sulphuric acid, concentrating to a small bulk and allowing it to cool. The sulphate crystallised out in bright, colourless plates. It was almost insoluble in cold water. It was recrystallised from hot water and the base then liberated by dilute alkali and washed until free from alkali. The dried base was washed with small quantities of ether, redissolved in a small amount of chloroform and crystallised by addition of petroleum ether. The substance forms colourless needles, m.p. 175°. It is easily soluble in alcohol, fairly soluble in chloroform, slightly soluble in ether and nearly insoluble in petroleum ether.

The mother-liquors from kurchicine were evaporated to dryness. The residue was dissolved in the smallest amount of chloroform and precipitated by petroleum ether. Only a small crop of crystals was obtained. The filtrate gave conessine, which on recrystallisation melted at 120°.

The alcoholic mother-liquor from the precipitate (A) was evaporated to dryness in vacuum. The residue was treated with 95% alcohol and a portion was found insoluble. The solution was filtered and evaporated to dryness in *vacuo*. The residue was dissolved in water, the alkaloid liberated by caustic soda and taken up with petroleum ether. The petroleum ether was removed and the base obtained as a soft, yelllowish mass, which gradually hardened on keeping. The crystallisation of the substance was a very long and tedious affair. The hydrochloride could only be obtained as an amorphous mass by passing dry hydrochloric acid gas in dry ethereal solution but it was very soluble in water and hygroscopic. The nitrate, phosphate, hydrobromide, tartrate, oxalate, all failed to crystallise. The crude base could not be made to crystallise from any solvent. After several trials, the sulphate was crystallised in

the following way: The base was dissolved in dilute sulphuric acid, the solution being kept neutral. It was concentrated below 60° under reduced pressure. On keeping the concentrated solution for 3 or 4 days, microscopic needles of the sulphate gradually separated. These were transferred to a Buchner funnel, washed with absolute alcohol and recrystallised from water. The pure sulphate was then dissolved in water, the alkaloid liberated by caustic soda and taken up with ether. The ethereal solution was dried with anhydrous sodium sulphate and on concentration gave tufts of white needles. The base melts at 75° and the m.p. is not altered by recrystallisation. Owing to the difficulty of crystallising this low-melting alkaloid, it could not be obtained in quantitative yield. This alkaloid forms, however, the largest proportion of the total alkaloids present in *Kurchee* bark and a study of its pharmacological action will determine the suitability of the bark as an economic product.

A study of the properties and some of the analytical results shows that kurchicine is quite different from holarrhenine. Holarrhenine melts at 197°-198°, while the m.p. of kurchicine after repeated crystallisation did not rise above 175°. The nitrogen content of holarrhenine is 7·56%, while that of kurchicine is 8·53% (average of 4 combustions). The specific rotation of holarrhenine in $CHCl_3$ is −7·1°, while that of kurchicine is nearly −10°. The specific rotation of holarrhenine hydrobromide, B. 2HBr. $3H_2O$, in water is +11·0°, while that of kurchicine hydrobromide (anhydrous) is −18·75°.

The low-melting alkaloid, for which the name "kurchine" is suggested, is also a new alkaloid (m.p. 75°). It is easily soluble in alcohol, chloroform, ether and petroleum ether. The nitrogen content was found to be 9·84% (average of 3 combustions), while that of conessine is 7·86%.

Summary.

(1) The content of alkaloids in Indian *Kurchee* bark is found to be about 1·2 per cent.

(2) A new method is described in detail for the separation of the individual alkaloids.

(3) Two new alkaloids, besides conessine, have been discovered and are designated kurchicine and kurchine respectively, the latter being present in the largest amount.

(4) Some decisive evidences for the two new alkaloids are adduced as a preliminary report.

(5) From the amount of the total alkaloids present, it will be quite economical to prepare salts of the alkaloids in a commercial scale, if the alkaloids give satisfactory clinical results.

(6) The method of separation devised will enable one to eliminate the more toxic alkaloid, if there be any.

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A Note on a New Method of Volumetric Estimation of Mercuric Oxide.

By Priyadaranjan Rây and Jyotirmoy Das-Gupta.

Mercuric oxide completely dissolves in sodium thiosulphate solution in the cold with liberation of an equivalent amount of alkali and formation of the complex mercury sodium thiosulphate. The reaction is a quantitative one and the amount of mercuric oxide in a sample can be easily determined by titrating the alkali disengaged. The excess of thiosulphate present does not interfere with the titration of the alkali. This furnishes a rapid method of evaluating mercuric oxide in commercial samples of the same, in basic salts of mercury and in various medicinal preparations. It has got sure advantages over the potassium iodide method of Rupp and Schirmer (*Pharm. Zeit.*, 1908, **53**, 928) being much less expensive ; the results are however equally good. The reaction involved is represented by the following equation :—

$$HgO+2Na_2S_2O_3=Na_2[Hg(S_2O_3)_2]+2NaOH.$$

Experimental.

At first a known amount of alkali was taken mixed with different quantities of sodium thiosulphate solution and titrated with standard acid. The results are tabulated below :—

Alkali taken.	N/5 Thiosulphate added.	Acid required.
25 c.c.	0 c.c.	25·25 c.c.
,,	0 ,,	25·25 ,,
,,	10 ,,	25·25 ,,
,,	20 ,,	25·25 ,,
,,	30 ,,	25·3 ,,
,,	40 ,,	25·3 ,,

The results indicate that the presence of thiosulphate has no effect on the alkali titration.

To determine the strength of the mercuric oxide a weighed amount of the substance was taken and estimated by the potassium iodide method. Thus a weighed amount of mercuric oxide was dissolved in excess of potassium iodide solution and the liberated caustic soda was titrated with N/10 sulphuric acid (f=0·9700). Results are given below.

HgO taken.	Acid required.	Hg found.	Percentage.
·2109 gms.	20·25 c.c.	·19642 gms.	93·1
·2673 ,,	25·6 ,,	·24832 ,,	92·9

A weighed amount of mercuric oxide was taken in each case. This was dissolved in the cold in excess of thiosulphate solution and the liberated caustic soda as titrated with N/10 sulphuric acid. In each case the total volume of the solution was maintained at or about 150 c.c. with varying amounts of thiosulphate, the results of which are tabulated below:—

TABLE I.

NaOH titrated with N/10 sulphuric acid (f=0·9700).

HgO taken.	Acid required.	Hg found.	Per cent.	Thiosulphate added.
·0865 gms.	8·3 c.c.	·08051 gms.	93·07	2 gms.
·1958 ,,	18·8 ,,	·18236 ,,	93·13	,,
·2022 ,,	19·4 ,,	·18818 ,,	93·2	,,
·2094 ,,	21·1 ,,	·19497 ,,	93·1	,,
·3575 ,,	34·3 ,,	·33281 ,,	93·09	,,
·2388 ,,	22·9 ,,	·22213 ,,	93·14	,,

TABLE II.

HgO taken.	Acid required.	Hg found.	Per cent.	Thiosulphate added.
·2161 gms.	20·65 c.c.	·20003 gms.	93·15	4 gms.
·2759 ,,	26·5 ,,	·25705 ,,	93·17	,,
·2655 ,,	25·5 ,,	·24735 ,,	93·16	,,
·2943 ,,	28·25 ,,	·27402 ,,	93·1	,,

TABLE III.

HgO taken.	Acid required.	Hg found.	Percentage.	Thiosulphate added.
·2606 gms.	25·1 c.c.	·24347 gms.	93·4	6 gms.
·1745 ,,	16·8 ,,	·16296 ,,	93·3	,,
·1408 ,,	13·55 ,,	·131435 ,,	93·3	,,

TABLE IV.

HgO taken.	Acid required.	Hg found.	Per cent.	Thiosulphate added.
·1238 gms.	11·9 c.c.	·11543 gms.	93·5	7·5 gms.
·2503 ,,	24·1 ,,	·23377 ,,	93·39	,,
·3240 ,,	31·2 ,,	·30264 ,,	93·3	,,

Pure mercuric oxide contains 93·06 per cent. of mercury.

It should be pointed out here that too much excess of thiosulphate makes the end point less sharp and renders the result a little high as shown in Table III and IV. The presence of too much excess of thiosulphate in the solution therefore should be carefully avoided.

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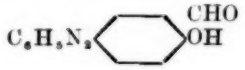
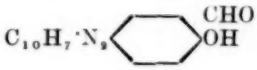
Azo-triphenylmethane and Azo-pyronine Dyes (Meta Series).

By Rajendra Nath Sen and Benoybhushan Ghosh.

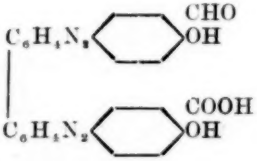
The present paper deals with azo-triphenylmethane dyestuffs containing azo and triphenylmethane groups in the *meta* position to one another, the object being to study the relative influence of the two chromophores in the *meta* positions as has been done in the case of the *para* positions by previous workers (Green and Sen, *J. Chem. Soc.*, 1912, **101**, 1113; Sen and Sett, *J. Am. Chem. Soc.*, 1924, **46**, 111; Dutt, *J. Chem. Soc.*, 1926, **129**, 1171). The *meta* azoalde-hydes (A, B, C, D) used in the preparation of the required azotriphenylmethane dyes, have been obtained by coupling salicylaldehyde with the corresponding diazotised amines, of which only (A) seems to have been prepared before (Tummeley, *Annalen*, 1889, **251**, 174; Borsche, *Ber.*, 1900, **33**, 1325).



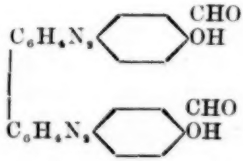
(A)



(B)



(C)



(D)

The above azo-aldehydes have been condensed (*i*) with dimethyl-aniline and *o*-cresotinic acid to give azo-triphenylcarbinol dyes and (*ii*) with resorcinol, pyrogallol and diethyl-*m*-aminophenol to give azo-pyronine dyes.

From a comparison of the various azo-triphenylcarbinol and azo-pyronine dyes prepared, it has been found (*vide* Table) that (1) the introduction of one azo group in the *meta* position to the central

carbon atom in a triphenylcarbinol or a pyronine dye is generally attended with an increase in the depth of colour much less than in the case of *para* position ; (2) introduction of a second azo group intensifies that colour still more though to a small extent ; (3) introduction of another triphenylcarbinol group into a molecule containing two azo and one triphenylcarbinol groups is, however, attended with a diminution in the intensity of colour. The leuco condensation products of *o*-cresotinic acid with (C) and (D) are substantive to cotton like the azo-aldehydes themselves, though slightly lighter in colour, while the corresponding carbinols have little or no direct affinity for cotton. Disappearance of the substantive character of the dyestuffs may thus be attributed to the triphenylcarbinol group in its quinonoid form. The other triphenylcarbinol and pyronine dyestuffs derived from (C) and (D) have also no direct affinity for cotton.

A great difference between the azo-triphenylmethane dyes of the *para* and the *meta* series is that the yellow shade on wool produced by the leuco cresotinic acid compounds of the *para*-series changes from yellow through maroon to dark green and black by after-chroming and the carbinols are remarkably polygenetic (Green and Sen, *loc. cit.*), but the yellow shade produced by the corresponding leuco-compounds in the *meta*-series changed only to olive brown on similar treatment and the carbinols are only feebly polygenetic.

Experimental.

Benzene-azo-salicylaldehyde (A) was prepared by the method of Tummeley (*loc. cit.*), and obtained as golden yellow prisms from dilute alcohol, melting at 127°.

Naphthalene-azo-salicylaldehyde (B).—A solution of diazotised α-naphthylamine (14·3 g.) is poured into an alkaline solution of salicylaldehyde (14 g.) and the mixture is stirred for an hour. The precipitated azo compound is filtered, washed and dried. It is obtained as a microcrystalline yellowish orange powder from dil. alcohol. It is soluble in alcohol, ether, benzene, chloroform etc.

The *phenylhydrazone*, prepared in glacial acetic acid solution at the temperature of the water-bath, crystallised from dil. alcohol ; m. p. 96°. (Found: N, 15·01. $C_{23}H_{18}ON_4$ requires N, 15·30 per cent.).

The *oxime* was prepared by adding a strong aqueous solution of hydroxylamine hydrochloride and sodium acetate to an alcoholic solution of the aldehyde and heating for 2 hours on the water-bath. The precipitate obtained on dilution is crystallised from dil. alcohol ; m. p. 201° (Found: N, 14·68. $C_{17}H_{13}O_4N_3$ requires N, 14·43 per cent.).

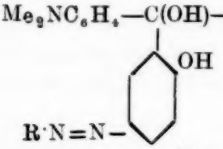
Diphenyl-disazo-salicylic acid-salicylaldehyde (C).—A diazotised solution of benzidine (9·2 g.) is added to a cold solution of salicylic acid (7·2 g.) in Na_2CO_3 (23 g.) and 250 c. c. of water. The mixture is stirred for 3-4 hours. The formation of the intermediate compound is complete when the solution no longer gives blue colour with alkaline "H" acid. To this mixture a cold solution of one mol. of salicylaldehyde (6·5 g.) in NaOH is now added and the stirring continued for another 4-5 hours, the completion of the reaction being tested with alkaline β-naphthol. The precipitated azo-compound is then filtered, washed and dried. It is obtained as a microcrystalline yellowish orange powder from hot nitrobenzene solution. It is insoluble in almost all solvents except nitrobenzene and pyridine.

Oxime.—It was prepared by adding a strong aqueous solution of hydroxylamine hydrochloride and sodium acetate to a solution of the aldehyde in pyridine and heating on the water-bath for 3-4 hours. It crystallised from dilute pyridine. It does not melt below 300°. (Found: N, 14·64. $C_{30}H_{19}O_5N_5$ requires N, 14·55 per cent.).

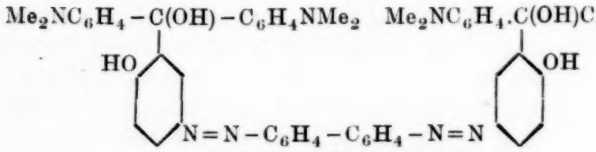
Diphenyl-disazo-bis-salicylaldehyde (D).—A diazotised solution of benzidine (9·2 g.) is poured into a cold solution of salicylaldehyde (6·5 g.) in Na_2CO_3 (23 g.) and water (100 c. c.) and the mixture is stirred for 3-4 hours. When the coupling with one mol. of salicylaldehyde is complete (the mixture being tested as in the above case), a second mol. of salicylaldehyde (6·5 g.) dissolved in the minimum quantity of NaOH solution is added and the stirring continued until the reaction is complete. The precipitated azo compound is filtered, washed and dried. It is obtained as a microcrystalline yellow powder from hot nitrobenzene solution. It is insoluble in all solvents except nitrobenzene and pyridine.

The *dioxime* was prepared as in the last case. It does not melt below 300°. (Found: N, 17·32. $C_{30}H_{20}O_4N_6$ requires N, 17·5 per cent.).

(5, 6, 7 and 8). *Condensations of the Azo-aldehydes with Dimethylaniline.*



(In the case of a monoaldehyde A, B or C)

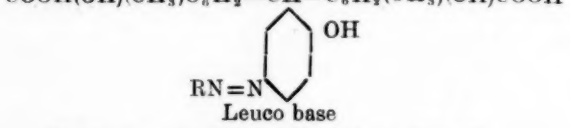


(In the case of a dialdehyde D).

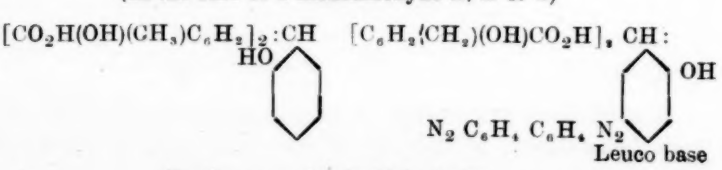
One mol. of the aldehyde mixed with the required quantity of dimethylaniline (2 mols. in the case of a monoaldehyde and 4 mols. in the case of a dialdehyde) and a small quantity of conc. HCl is heated for 5-6 hours, at 100° in the case of the aldehydes (A) and (B) and at 120° in the other two cases. The leuco-compound is isolated in the usual way and finally crystallised from chloroform. It is insoluble in ether and benzene, slightly soluble in alcohol and acetone, freely soluble in chloroform.

The leuco compound is oxidised to the carbinol stage by adding lead peroxide to a solution of the former in a mixture of dil. HCl and dil. acetic acid in the cold.

(9, 10, 11 and 12). *Condensations of the Azo-aldehydes with o-Cresotinic Acid.*



(In the case of a monoaldehyde A, B or C)

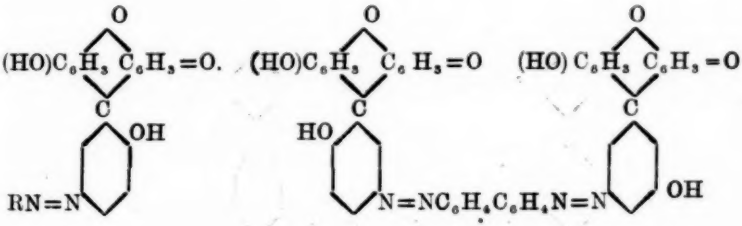


(In the case of a dialdehyde D)

One mol. of the azo-aldehyde is intimately mixed with the required quantity of dry *o*-cresotinic acid (2 mols. in case of a monoaldehyde and 4 mols. in the case of a dialdehyde) and the mixture is dissolved in the minimum quantity of conc. H_2SO_4 (*d* 1·84). It is kept overnight and then washed with ice-cold water to remove the H_2SO_4. The product is now dissolved in NaOH solution, filtered, reprecipitated with dil. HCl and again filtered. It is then dried and the finely powdered product is purified by washing with benzene and is finally crystallised from dil. alcohol, when the leuco-compound is obtained as a microcrystalline yellow powder. It is insoluble in ether and benzene, but soluble in alcohol, acetone, chloroform etc.

The carbinol is obtained by condensing the aldehyde with cresotinic acid in the cold as above and then adding the requisite quantity of nitrosyl sulphate ($NaNO_2$ dissolved in cold conc. H_2SO_4) to the mixture and heating to 60°-70° till the oxidation is complete. The product is then isolated in the manner already described and finally purified by repeated washing with alcohol in which it is insoluble. It may be crystallised from pyridine.

(13, 14, 15 and 16). *Condensations of the Azo-aldehydes with Resorcinol.*



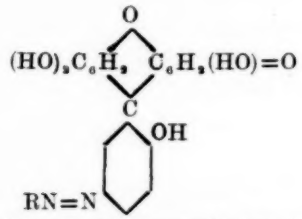
(In the case of a monoaldehyde A, B or C)

(In the case of a dialdehyde D)

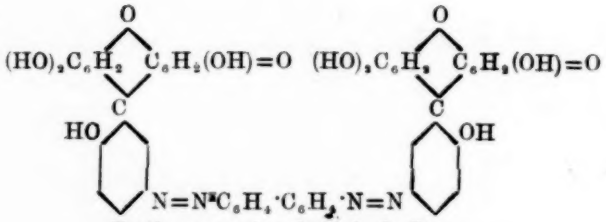
One mol. of the aldehyde mixed with resorcinol (2 mols. in the case of a monoaldehyde and 4 mols. in the case of a dialdehyde)

is dissolved in the minimum quantity of conc. H_2SO_4 (*d* 1·84) and kept at about 120° for 5-6 hours. During the reaction sulphur dioxide is evolved (detected with starch-iodate paper) sulphuric acid acting as condencing as well as oxidising agent. The mixture is cooled and then washed with ice-cold water. The product is then dissolved in NaOH solution, filtered, reprecipitated with dilute HCl, again filtered, washed and dried. The powdered product is then purified by repeated washing with alcohol and other solvents in the case of the products from (A) and (B) and with hot nitrobenzene and ether in the case of the products from (C) and (D), these products being insoluble in all ordinary solvents.

(17, 18, 19 and 20). *Condensations of the Azo-aldehydes with Pyrogallol.*



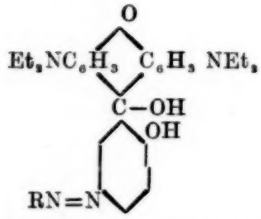
(In the case of a monoaldehyd A, B or C)



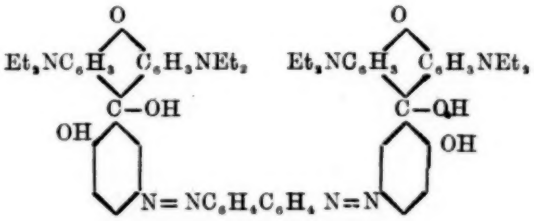
(In the case of a dialdehyde D)

The method of preparation is similar to that followed in the case of condensation with resocrinol. These compounds are also insoluble in all ordinary solvents.

(21, 22, 23 and 24). *Condensations of the Azo-aldehydes with Diethyl*-m-*aminophenol.*



(In the case of a monoaldehyde A, B or C.)



(In the case of a dialdehyde D).

One mol. of the aldehyde mixed with dry diethyl-*m*-aminophenol (2 mols. in the case of a monoaldehyde and 4 mols. in the case of a dialdehyde) is dissolved in the minimum quantity of conc. H_2SO_4 (*d* 1·84) and kept at about 140° for 6-7 hours. Sulphur dioxide being evolved during the course of the reaction. The mixture is allowed to cool and extracted with cold water. To the filtered aqueous solution ammonium hydrate is added and the preciptiate is filtered, washed and dried. It is then purified by washing with benzene and finally crystallised from dil. alcohol. It is insoluble in ether and benzene, but soluble in alcohol, acetone, chloroform and nitrobenzene.

The properties and analyses of the compounds prepared and studied are given in the annexed table.

TABLE.

	Names of compounds.	Melting point.	Analysis: P.c. of N.		Shade on wool and silk.	Remarks.
	Azo-aldehyde.		Found.	Calc.		
1.	A.	127°	—	—	Yellow	
2.	B.	151°	10·23	10·14	Yellowish orange.	
3.	C.	Does not melt below 300°	12·12	12·02	,, ,,	Also substantive to cotton.
4.	D.	Do.	12·23	12·44	,, ,,	
	Cond. products (leuco) of dimethyl-aniline with the azo-aldehydes.					
5.	A.	Melts with decomposition.	—	—	Greenish blue	No. 5 prepared before by Dutt (*loc. cit.*).
6.	B.	,,	10·81	10·20	Green	Shades produced by carbinols. These also dye tannined cotton.
7.	C.	,,	11·66	12·17	Greenish blue	7 and 8 have no direct affinity for cotton like the mother substances C & D.
8.	D.	,,	12·11	12·47	,, ,,	

1. Benzene-azo-salicylaldehyde;
2. Naphthalene-1-azo-salicylaldehyde;
3. Diphenyl-disazo-salicylic acid-salicylaldehyde;
4. Diphenyl-disazo-bi-salicylaldehyde;
5. 2-Benzene-azo-5-hydroxy-8 : 13-tetramethyldiamino-triphenyl-methane;
6. 2-Naphthalene-azo-5-hydroxy-8 : 13-tetramethyldiamino-triphenyl-methane;
7. Diphenyl-disazo-salicylic acid-5-hydroxy-8 : 13-tetramethyldiaminotriphenylmethane;
8. Diphenyl-disazo-bi-(5-hydroxy-8 :13-tetramethyldiamino-triphenylmethane);

Names of compounds.		Melting point.	Analysis : P.c. of N.		Shade on wool and silk.	Remarks.
Cond. products (leuco) of *o*-cresotinic acid with the azo-aldehydes.			Found.	Calc.		
9.	A.	212°	5·24	5·47	Reddish orange.	Shades produced by carbinols. The corresponding carbinols in the *para*-series (Green and Sen, *loc. cit.*) produce red shades. All the carbinols are feebly polygenetic. The leuco compounds produce shades similar to the aldehydes. The leuco compounds 11 & 12 are like the mother substances C & D substantive to cotton but their carbinols have little or no direct affinity for cotton.
10.	B.	159°	4·71	4·98	,, ,,	
11.	C.	Does not melt below 300°.	7·52	7·45	,, ,,	
12.	D.	Do.	5·13	5·48	,, ,,	
Cond. products of resorcinol with the azo-aldehydes.						
13.	A.	Does not melt below 300°.	6·15	6·86	Brownish red	Alkaline solutions feebly fluorescent. Resorcinol-1′-hydroxybenzene (Sen & Sinha, *J. Am. Chem. Soc.*, 1923, **43**, 2984) produces only orange shades and its alkaline solution is strongly fluorescent thus the azo-group in the *meta* position increases the depth of colour but diminishes fluorescence. 15 slightly deeper than 13. 16 is slightly lighter than 15. 15 & 16 unlike C & D have no direct affinity for cotton.
14.	B.	Do.	5·79	6·11	Red	
15.	C.	Do.	8·14	8·64	Brownish red	
16.	D.	Do.	6·24	6·88	Brown	

9. 2-Benzeneazo-5 : 8 : 13-trihydroxy-9 : 12-dimethyl-7 : 14-dicarboxytriphenylmethane;
10. 2-Naphthalene-α-azo-5 : 8 : 13-trihydroxy-9 : 12-dimethyl-7 : 14-dicarboxy-triphenylmethane;
11. Diphenyl-disazo-salicylic acid-5 : 8 : 13-trihydroxy-9 : 12-dimethyl-7 : 14-dicarboxy-triphenylmethane;
12. Diphenyl-disazo-bi-(5 : 8 : 13-trihydroxy-9 : 12-dimethyl-7 : 14-dicarboxy-triphenylmethane);
13. Benzene-azo-resorcinol-salicein;
14. Naphthalene-α-azo-resorcinol-salicein;
15. Diphenyl-disazo-salicylic acid-resorcinol-salicein;
16. Diphenyl-disazo-bi-resorcinol-salicein;

Names of compounds.		Melting point.	Analysis : P.c. of N.		Shade on wool and silk.	Remarks.
			Found.	Calc.		
Cond. products of pyrogallol with the azo-aldehydes.						
17.	A.	Does not melt below 300°.	5·69	6·36	Greyish black	Shades on iron-mordanted wool. All feebly palygenetic. 19 & 20 unlike C & D have no direct affinity for cotton.
18.	B.	Do.	5·20	5·71	,,	
19.	C.	Do.	—	—	,,	
20.	D.	Do.	—	—	,,	
Cond. products of diethyl-*m*-aminophenol with the azo-aldehydes.						
21.	A.	185°	9·89	10·45	Violet	Also dye tannined cotton. 23 slightly deeper than 21. 24 slightly lighter than 23. 23 & 24 unlike C & D have no direct affinity for cotton.
22.	B.	Does not melt below 300°.	9·10	9·56	Bluish violet	
23.	C.	Do.	10·56	10·82	,,	
24.	D.	Do.	10·08	10·47	Violet	

17. Benzene-azo-pyrogallol salicein ;
18. Naphthalene-α-azo-pyrogallol-salicein ;
19. Diphenyl-disazo-salicylic acid-resorcinol-salicein ;
20. Diphenyl-disazo-bi-pyrogallol-salicein ;
21. Benzene-azo-diethyl-*m*-aminophenol-salicein ;
22. Naphthalene-α-azo-diethyl-*m*-aminophenol-salicein ;
23. Diphenyl-disazo-salicylic acid-diethyl-*m*-aminophenol-salicein ;
24. Diphenyl-disazo-bi-(diethyl-*m*-aminophenol-salicein). (The compounds have been named according to the system of nomenclature used in "Systematic Survey of Organic Colouring Matters" by Green).

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Magnetic Properties of Complex Compounds and their Electronic Constitution.

By Priyadaranjan Rây and Harigopal Bhar.

Of recent years many attempts have been made to correlate the magnetic properties and the electronic constitution of complex inorganic compounds. Of these mention may be made of those by Cabrera (*J. Phys. Radium*, 1925, **6**, 276) supported by Jackson (*Phil. Mag.*, 1926, **2**, 87 ; 1927, (*vii*) **4**, 1070), Welo and Baudisch (*Nature*, 1925, **116**, 606), Bose (*Zeit. Phys.*, 1925, **35**, 213, 219), Lessheim, Meyer and Samuel (*Zeit. anorg. Chem.*, 1927, **165**, 253) and Rây (*J. Indian Chem. Soc.*, 1928, **5**, 73). A critical examination of all these views from chemical standpoint has been made by one of us Rây (*loc. cit.*). In order to further test the validity of these different views we undertook the measurement of magnetic susceptibilities of a variety of complex compounds, the results of which are embodied in the present paper and form the basis of discussion raised herein. We will however pass over Lessheim and his coworkers' view as it could not be reconciled with our present conception of valency. This has already been pointed out by Rây (*loc. cit.*).

Both Welo-Baudisch and Bose assume that the magnetic properties depend primarily on the "effective atomic number" of the central atom of the complex ion as defined and interpreted by Sidgwick (*J. Chem. Soc.*, 1923, **123**, 725). They have also adduced some evidences in support of their views. According to these views a complex becomes diamagnetic when its effective atomic number is equal to the atomic number of an inert gas ; and when this number for the complex differs from that of the next inert gas by n units, the complex becomes paramagnetic with a magnetic moment corresponding to n Bohr magnetons (Bose, *loc. cit.*). But this rule does not hold good in the case of complex ions formed by zinc and cobaltous cobalt. Welo and Baudisch do not give any definite distribution of electrons in different sub-groups giving rise to co-ordination bonds ; whereas Bose has given a scheme for the same which howeverfails to account for all the chemical properties of the complex

as has already been pointed out by Rây (*loc. cit.*). Cabrera assumes that co-ordinating electrons are arranged in two groups of 4 or 6 each depending on the nature of the co-ordination in an external quantum group and they contribute nothing to the magnetic moment. It is further implied in Cabrera's scheme that paramagnetism in complex ions develops when any sub-group in the main quantum group of the central atom does not contain its full quota of electrons ; consequently a completed or vacant sub-group develops diamagnetic property. Rây also holds the same view which was first formulated by Ladenburg (*Naturwiss.* 1920, **8**, 6) ; but Rây has distinguished two types of complexes, penetration or perfect and associated or imperfect complexes depending on the nature of their electronic configuration. However, both Cabrera and Rây do not stick to any definite rule regarding the magnetic moments of paramagnetic complexes as enunciated by Bose.

We shall now proceed to discuss the results of our measurements of magnetic susceptibilities of a variety of complex compounds on the basis of these four different views in order to determine which of them best explains the experimental values. The measurements were all made in the solid state by means of a Curie's balance with conductivity water as the standard and at the room temperature (25-34°). The specific or mass susceptibility of water is taken as $\chi_m = -0{\cdot}72 \times 10^{-6}$.

As our object was to determine the nearest Bohr magneton value for the paramagnetic complexes and also the magnetic nature of the complex itself (dia- or para-magnetic) we did not take sufficient pains to obtain magnetically pure (apart from chemically pure) samples in all cases, specially in the case of certain unstable compounds as will be indicated later on. So in those cases our experimental results should be regarded as giving more or less approximate values and consequently we do not claim any high degree of accuracy for them.

Further, in calculating the magneton number we have ignored the effect of diamagnetic atoms and ions, as they have already been found by Rosenbohm (*Zeit. physikal. Chem.*, 1919, **93**, 693) to exert negligible influence so far as our present purpose is concerned.

The results of measurements are given in the accompanying table.

Results of susceptibility measurements.

No.	Substance.	Temperature (Centigrade.)	$\chi_m.10^6$	nWeiss.	nBohr (nearest)	nBohr (theoretical, calc. after Welo and Bose's rule).
1.	$CoCl_2.2N_2H_4$	25°	48·7	23·6	4	3
2.	$Co(SCN)_2.2N_2H_4$	27°	37·0	22·9	4	3
3.	$CoSO_4.3N_2H_4$	26°	35·9	23·0	4	1
4.	$CoSO_3.2N_2H_4.H_2O$	26°	33·6	20·9	3-4	3
5.	$Co(CH_3.COO)_2.2N_2H_4$	25°	33·2	21·7	3-4	3
6.	$Co(SCN)_2.4C_5H_5N$	26°	18·6	23·2	4	3
7.	$NiCl_2.2N_2H_4$	26°	18·1	14·4	2	2
8.	$NiCl_2.3N_2H_4$	26°	13·9	13·6	2	2
9.	$NiSO_3.2N_2H_4.2H_2O$	27°	14·8	14·5	2	2
10.	$Ni(NO_3)_2.2N_2H_4$	25°	16·2	14·3	2	2
11.	$NiSO_3 3N_2^{\gamma}H_4.H_2O$	27°	11·6	13·2	2	2
12.	$FeCl_2.2N_2H_4$	25°	57·7	23·4	4	4
13.	$Ni(C_4H_7N_2O_2)_2$ (Nickel dimethylglyoxime)	27°	0·10	1·3	...	2
14.	$Ni(C_2H_5ON_4)_2.2H_2O$ (Nickel dicyandiamidine)	...	−0·32	...	Dia	2
15.	$Ni(C_2S_2N_2H_2)$ (Nickel rubeanate, Rây and Ray, *J. Indian Chem. Soc.*, 1926, 3, 118).	29°	0·28	1·7	...	2
16.	$K_2Ni(CN)_4.H_2O$	...	−0·362 −0·57(B)	Dia	Dia	2
17.	$K_2Ni(CN)_4$	...	−0·261 −0·49(B)	Dia	Dia	2
18.	$\left[Co\begin{matrix}(NH_3)_5\\(NO)\end{matrix}\right]Cl_2$ (black)	29°	13·3	13·9	2	2
19.	$\left[Co\begin{matrix}(NH_3)_5\\(NO)\end{matrix}\right](NO_3)_2.\frac{1}{2}H_2O$ (red)	...	−0·109	Dia	Dia	Dia
20.	$K\left[Fe\begin{matrix}(NO)_2\\S_2O_3\end{matrix}\right]H_2O$	30°	0·0245	0·6	...	...

No.	Substance.	Temperature (Contigrade)	$\chi_m.10^6$	ηWeiss	ηBohr (nearest)	ηBohr (Theoretical, calc. after Welo and Bose's rule).
21.	$K_2Fe_3(NO)_{14}S_6.2H_2O$	28°	0·159	1·2	...	...
22.	$KFe(NO)_2S.3H_2O$	25°	0·54	2·8	...	...
23.	$Na_2\left[Fe\begin{matrix}(NO)\\(CN)_5\end{matrix}\right]2H_2O$	...	−0·31 −0·35 (Welo, *loc. cit*)	Dia	Dia	Dia
24.	$K_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	...	−0·362	,,	,,	,,
25.	$(NH_4)_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	...	−0·372	,,	,,	,,
26.	$Rb_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	...	−0·546	,,	,,	,,
27.	$Cs_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	...	−0·299	,,	,,	,,
28.	$Na_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]H_2O$	...	−0·303	,,	,,	,,
29.	$Tl_4\left[Co\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right]$	...	−0·181	,,	,,	,,
30.	$\left[Co\begin{matrix}S_2O_3\\(NH_3)_5\end{matrix}\right]Cl$	...	−0·291	,,	,,	,,
31.	$K_3Co(CN)_6$	...	−0·320 −0·37(B)	,,	,,	,,
32.	$K_4Co(CN)_6$	...	−0·398	,,	,,	1
33.	$K_6\left[Co_2\begin{matrix}SO_3\\(CN)_{10}\end{matrix}\right]$	...	−0·407	,,	,,	Dia
34.	$Co(C_2S_2N_2H_2)\cdot 2H_2O$	3·1	15·6	14·1	2	3
35.	$K_4Mn(CN)_6.3H_2O$	23°	4·1	10	1	1
36.	$K_3Mn(CN)_6$	25°	10·8 16·7(B)	14·5 18(B)	2 3 (B)	2
37.	$Cu(C_2H_5ON_4)_2.3H_2O$ Copper dicyandiamidine	29°	3·3	7·9	1	1
38.	$Cu(C_2NO_2H_4)_2.H_2O$ Copper aminoacetate.	28°	5·1	8·3	1	1

No.	Substance.	Temperature (Centigrade).	$\chi_m.10^6$	ηWeiss	ηBohr (nearest)	ηBohr (Theoretical, calc. after Welo and Bose's rule).
39.	$KCu(CN)_2$	...	−0·287	Dia	Dia	...
40.	$K_4Cr(CN)_6.2H_2O$	30°	11·4	16·5 (?)	2	2
41.	$K_3Cr(CN)_6$	26°	15·5 20(B)	17·2 19(B)	3 3(B)	3
42.	$K_3MoCl_6.2H_2O$	25°	13·1	17·6	3	3
43.	$(NH_4)_3Mo(SCN)_6.4H_2O$	25°	9·5	17·8	3	3
44.	$K_4Mo(CN)_8.2H_2O$	...	−0·295 −0·48(B) (anhydrous)	Dia	Dia	Dia
45.	$K_3W(OH)Cl_5$	31°	4·0	8·6	1	4
46.	$K_3W_2Cl_9$	...	−0·265	Dia	Dia	...
47.	$K_4W(CN)_8.2H_2O$	...	−0·36 −0·43(B) (anhydrous)	Dia	Dia	Dia

where χ_m=mass susceptibility; η_{Weiss}=Weiss magneton number and ηBohr=Bohr's magneton number.

Since this paper was communicated a paper by Biltz (*Zeit. anorg. Chem.*, **1928**, **170**, 161) reached us here; in this paper he has also given the results of susceptibility measurements of a few of the above compounds. His values though slightly differing from ours are quite comparable for our present purposes except in the case of the compound No. 36, where a serious and large discrepancy is noted. But in this latter case we have no reasons to doubt our own value. His values are indicated in the table by the symbol B.

Of the six cobaltous complexes examined (nos.1—6 *cf.* Table) four give values almost equal to 4 Bohr magnetons. One of these four is a sixfold and the other three are fourfold co-ordination complexes. The magnetic moment of these complexes approaches the value (ηWeizs=24·56) for the simple cobaltous salts. The remaining two give values between 3 to 4 Bohr magnetons.

Cobaltous complexes are regarded by Rây only as associated complexes wherein the distribution of electrons in the simple cobaltousion is left unchanged. As for the other two compounds nos. 4 and 5 it may be assumed that we are dealing here with mixtures

in which a small proportion has the tendency to assume a more perfect type resembling Rây's penetration complexes which leads to a rearrangement of electrons reducing the magnetic moment to a certain extent.

Of the five nickel complexes examined (nos. 7—11), all give values approximately equal to 2 Bohr magnetons, but always slightly lower than the value for the simple nickel ion which is equal to 16—17 Weiss magnetons. The compound no. 12 which is a ferrous complex of the associated type gives a value almost equal to 4 Bohr magnetons which is only slightly lower than that for the simple ferrous salts (26·0 Weiss). The slight excess of the magneton values in the case of both the simple nickelous and ferrous salts over the integral Bohr magneton values may be explained as due to their containing mixtures of isomeric ions caused by a difference in the arrangement of outer electrons in the M_3 level of the atom.

Of the five nickel complexes of the fourfold type (nos. 13—17), only the compounds nickel dimethyl glyoxime and nickel rubeanate possess a very small residual paramagnetism amounting approximately to only one Weiss magneton. So, for our present purpose they may be regarded as practically diamagnetic. Potassium nickelocyanide both in the hydrated and anhydrous conditions are diamagnetic. The magnetic properties of sodium and potassium nickelocyanides were also studied by Depold (*vide* Jackson, *Phil. Mag.*, 1927, **4**, 1073) who also found them to be diamagnetic. These results cannot in any way be explained by Welo and Baudisch's and by Bose's views. Cabrera's view also fails to account for such anomalous results. In order to explain the diamagnetic character of sodium and potassium nickelocyanides on the basis of Cabrera's view, Jackson (*loc. cit.*) however suggests that in their cases a rearrangement of electrons in the nickel ion takes place. But what is the reason for such rearrangement and why does such rearrangement take place in only a few nickel complexes have not been stated. According to Rây's view we may regard that the nickelous ion can form both association and penetration complexes depending on the nature of the co-ordinating groups. With strongly polar groups or ions, it may reasonably be assumed that nickel can form perfect or penetration complexes, though usually it forms association complexes. The diamagnetic character of the above nickel

compounds may be ascribed to the formation of such perfect complexes. The electronic configuration for such a perfect complex may be represented by the following scheme:

	Electrons in K_{11} to M_{22} levels.	M_{23}	M_{33}	N_{11}	N_{21} N_{22}
Ni^{++}complex, perfect type (fourfold)	18	4	6	...	6

Every four of six electrons in M_{33} and N_1 levels are coupled and form the co-ordination bonds. Such configuration would evidently give rise to diamagnetic property.

It also incidentally confirms the complex character of nickel rubeanate as was established by Rây and Ray (*loc. cit.*) from a study of its chemical and other physical properties

Of the five nitroso compounds examined (nos. 18—23) nos. 18 and 22 which are rather unstable were evidently not in a magnetically pure condition. The values observed should therefore be regarded only as approximate ones. The object of these measurements is to determine the behaviour of the -NO group in the complex. According to Sidgwick an -NO group inside the complex furnishes three electrons to the central atom, one by transfer and two by sharing. Besides, the idea that the NO molecule can part with three electrons is supported by the theory of the nature of non-polar molecules as deduced from band spectra (*cf.* Johnson, *Sci. Progress*, *Oct.* 1927, p. 246), according to which the structure of NO molecule is similar to that of aluminium containing three valence electrons outside the L-shell. The diamagnetism of sodium nitroprusside, a ferric complex, has been explained on this basis. The black compound no. 18 can be represented as

$$\left[\begin{matrix}\mathrm{Co} & \mathrm{NO} \\ & (\mathrm{NH_3})_5\end{matrix}\right]\mathrm{Cl_3}$$

where the cobalt atom has been proved to behave as bivalent (*cf.* Werner and Karrer, *Helv. Chim. Acta*, 1918, **1**, 54). The observed susceptibility of the compound agrees however with that demanded by Bose's rule.

It is well known that the black variety is unstable and passes into the red modification. The red variety of the nitrate is represented

by the formula $[(NH_3)_5 Co-N_2O_2-Co(NH_3)_5] (NO_3)_4$ and the cobalt atom is regarded as trivalent; the group N_2O_2 behaving as a residue of hyponitrous acid (*cf.* Werner and Karrer, *loc. cit.*). Assuming the red compound to be a cobaltic complex and the bivalent acid radicle N_2O_2 to furnish one electron to each cobalt atom to form one co-ordination bond in each case, the effective atomic number of each cobalt atom in the complex becomes equal to 36, the number for the inert gas krypton and thus makes it diamagnetic.

It is however difficult to explain the value of the magnetic moment for the black modification of $CoCl_3. 5NH_3.NO$ according to Cabrera's and Rây's schemes. But as this compound is rather very unstable it seems that it is a mixture of two different forms with the cobalt atom in two different states of oxidation,—that is a mixture of an associated cobaltous complex with a perfect cobaltic complex, and the magnetic moment consequently lies between the values characteristic for the two. Still however, the magnetic moment corresponding to exactly two Bohr magnetons is significant.

The compounds nos. 20, 21 and 22 have a small paramagnetic moment ranging from 0·6 to 3 Weiss magnetons approximately. The constitution of these compounds are still obscure, specially the valency of iron. So it is very difficult to ascribe any electronic configuration to the co-ordinating iron atom or to determine the function of the -NO group. It can however be stated with reason from the very low values of their magnetic moments approximating to zero that they are more or less perfect type of complexes.

The compounds nos. 25 to 29 were lent to us by Rây and Moulik. The compound no. 31, potassium cobalticyanide could not be freed from traces of iron most probably present as potassium ferricyanide which is isomorphous with the cobalticyanide. Even starting with Merck's reagent cobaltnitrate, precipitating any trace of iron by means of ammonium chloride and ammonia, and then treating the filtrate with the purest sodium bicarbonate for the production of iron-free cobalt carbonate which was then treated with Merck's reagent potassium cyanide free from ferrocyanide, etc., and recrystallising the cobalticyanide obtained several times from conductivity water we found that the product still contained slight traces of iron. We have not as yet been able to trace the source of this iron. Probably it has been absorbed from the floating dust in the laboratory atmosphere. However the value of

the diamagnetic susceptibility given here represents the concordant result of three different preparations of the compound. We can therefore reasonably believe that when obtained absolutely pure it will manifest a little higher diamagnetic susceptibility. Incidently it indicates the difficulty of obtaining magnetically pure samples for which simple chemical analysis is no sure guide.

All the complex cobaltic compounds from nos. 24 to 31 are, as usual, diamagnetic. All the four views discussed above lead to the same result. A striking result has however been obtained with potassium cobaltocyanide (no. 32). This compound which is rather unstable has been found to give a diamagnetic susceptibility. Though the value of the susceptibility given above should be regarded as an approximate one on account of the instability of the compound which does not therefore permit of further purification, it can be definitely asserted that the compound is diamagnetic. Because paramagnetic property of any compound cannot be masked by the presence of a fairly large amount of diamagnetic impurities. According to Bose's and Welo's views potassium cobaltocyanide should give a magnetic moment equal to one Bohr magneton. Thus these views fail to explain its diamagnetic character. Cabrera's view is also incapable of explaining this anomalous result. Rây has however suggested in his paper (*loc. cit.*) that the last electron in potassium cobaltocyanide behaves as a valence electron and is pushed outside the level of the co-ordinating electrons. So under these circumstances the complex should behave magnetically similar to rubidium atom of atomic number 37. The mass susceptibility of Rb atom is quite small verging practically to diamagnetism ; the values for the mass and atomic susceptibilities of rubidium are $0{\cdot}07 \times 10^{-6}$ and $5{\cdot}97 \times 10^{-6}$ respectively (*cf.* Honda and Owen's Table in "Magnetism and Atomic Structure" by Stoner, p. 138). The Weiss magneton number for Rb atom is therefore practically negligible being approximately equal to 0·2 only. Hence it is not unreasonable to assume that potassium cobaltocyanide in a crystalline condition will exhibit diamagnetism. But it appears to us that a more probable explanation of the diamagnetism of potassium cobaltocyanide is this. In this complex we may regard one of the cyanogen ions to be linked by one electron only which it supplies to the central cobalt atom instead of a pair of electrons as usual. This produces an unstable condition impelling the central atom to readily lose one more electron resulting in the change of

the one electron bond into a two-electron co-ordinate bond, and the cobaltocyanide is oxidised to cobalticyanide—both the electrons being apparently supplied by the cyanogen group under consideration. On this assumption the magnetic behaviour of potassium cobaltocyanide as experimentally observed falls in a line with the views of Bose, Welo and Rây, though it is difficult to be represented by Cabrera's scheme. The high value of its diamagnetic susceptibility—higher than that of the very stable and perfect complex potassium cobalticyanide is certainly due to contamination with diamagnetic substances such as potassium cyanide, alcohol and ether. The substance was washed with alcohol and ether to avoid decomposition by water and could not be thoroughly dried for the same reason.

The compound no. 33 recently prepared by one of us (Rây) is a binuclear cobalt complex and is represented by the following formula by its author:—

$$K_6\,[(CN)_5Co-SO_3-Co(CN)_5].$$

μ-Sulphito-decacyanopotassium dicobaltiate.

In common with all the sixfold perfect cobaltic compiex this compound exhibits diamagnetism.

The compound no. 34 (cobalt rubeanate) furnishes another instance of anomalous magnetic behaviour. This compound was represented by its author (Rây and Ray, *loc. cit.*) as an inner-metallic cobaltous complex. It ought to give, according to Bose's rule, a magnetic moment of 3 Bohr magnetons. But it actually gives only 2 Bohr magnetons. Both Rây's and Cabrera's views which do not predict any definite quantitative measure of the magnetic moment, can however give electronic configurations for this compound. But it seems that the chemical constitution of the compound itself is not quite clear. Rây and Ray have already noticed that the two water molecules present in the componnd are not expelled even by heating to 130°. This suggest that the water molecules possibly form a part of the complex giving a sixfold instead of a fourfold complex. In any way the compound can reasonably be regarded as a mixture of two or more forms. That it approaches more or less a perfect complex is proved by the fact of its having a magneton number two Bohr units less than that of a simple cobaltous salt.

Compounds nos. 35 and 36 are the two complex mangano- and mangani-cyanides of potassium. Their susceptibilities are in conformity with the requirements of Bose's rule. According to Rây's view of the structure of sixfold complexes the electronic configurations for the two manganese complexes are given by the following scheme:

Substance.	Electrons in K_{11} to M_{22} levels.	M_{22}	M_{33}	N_{11}	N_{3}
$K_4Mn(CN)_6$	18	4	6	1	6
$K_3Mn(CN)_6$	18	3	6	1	6

Compounds nos. 37 and 38 should be regarded as Rây's association complexes, their magnetic moments remaining the same as for simple cupric salts. Compound no. 39 being a cuprous salt should be evidently diamagnetic.

Chromocyanide (no. 40) gives a value slightly higher than what conforms to Bose's rule. But as the compound is extremely unstable readily changing into chromicyanide specially at a temperature like 30°C (the laboratory temperature at the time of measurements), the observed value cannot represent the true magnetic moment of the compound in question.

The molybdenum compounds nos. 42 and 43 with the central atom of molybdenum in the trivalent condition behave like chromium complexes and like the latter obey Bose's rule. The compound no. 44, octacyano-potassium molybdenate with quadrivalent molybdenum as the central atom is diamagnetic as is to be expected, since being an eightfold complex its effective atomic number is equal to 54, the number for the inert gas xenon.

The tungsten compound no. 47 behaves exactly like the corresponding molybdenum compound. The effective atomic number of the central quadrivalent tungsten here is equal to 86, the number for the inert gas emanation or niton.

The tungsten compounds nos. 45 and 46 however give anomalous results. The compound $K_3W_2Cl_9$ is diamagnetic. In this the tungsten atom is trivalent. It is very difficult to explain its diamagnetic character on the basis of any of the views under discussion, as its constitution is obscure. Possibly in this case there is a direct linkage between the two tungsten atoms which give rise to complications. Again the compound $K_2W(CH)Cl_5$ exhibits a magnetic moment of one Bohr magneton. The tungsten atom is tetravalent here ; but it is very difficult to represent such a complex as having a magnetic moment of one Bohr magneton on any of the views under discussion.

The effective atomic number in this case is 74−4+12=82. This is a solitary case in which an even number of electrons gives an odd value of magneton number on the Bohr scale, and there is no reason to assume any of the co-ordination bonds as arising from the sharing of one electron only.

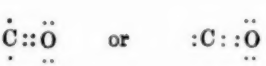
As a result of the above discussion of the values of magnetic moment of a variety of complex compounds communicated in this paper, it may be observed that Welo's and Bose's rules which claim to give a quantitative measure of the magnetic moment of a complex in terms of Bohr magneton number fail altogether in many well-known cases. It has also been found that Cabrera's scheme as well cannot account for the magnetic behaviour of a few well-defined complexes. On the whole Rây's view appears to explain satisfactorily the magnetic character of the largest number of complex compounds dealt with in this discussion. It is however noteworthy that whereas Bose enunciated his rule from a study of the magnetic properties of the complex compounds as far as investigated at the time, the rule, in spite of its failure in the cases of association complexes of cobalt and perfect complexes of nickel, has been evidently extended to the cases of nitroso-compounds of cobalt and cyanogen complexes of manganese. Finally, in view of the possibility of existence of different types of complexes as also their isomeric mixtures in a particular compound, an integral value of Bohr's magneton number cannot be always attributed to them.

Carbonyls of metallic elements *e.g.* $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ and $Mo(CO)_6$ present some interesting features. Nickel, iron and chromium carbonyls have been found to be diamagnetic. The character of molybdenum compound is not yet known. The effective atomic number of these carbonyl compounds being equal to the atomic number of the next inert gas, they should be diamagnetic according to Welo's and Bose's views. And their actual diamagnetic character is regarded as a strong evidence in support of their views. But it should be pointed out, as Jackson has done (*Phil. Mag.*, 1927, **4**, 1070), that in their representation of the configurations of these carbonyls they have assumed that each carbonyl group is co-ordinatively linked by a pair of shared electrons supplied by it to the central metallic atom. This however does not take into account the valence condition of the central atom. In other words the central atom is supposed to exercise its co-ordinating valency without exhibiting any of its normal or primary valency

This is rather unusual and contradictory to Werner's co-ordination theory of valency. Jackson has therefore represented them in a different way so that the valence condition of the central atom may also be easily recognised ; and he has tried to explain their diamagnetic character by attributing to them electronic configurations based on Cabrera's scheme. The compound nickel carbonyl is represented by him as $[Ni(CO)_3]CO$ and the iron carbonyl as $[Fe(CO)_4]CO$. This sort of representation is not quite satisfactory as it makes the carbonyl compounds electrolytes with a bivalent complex positive ion and a bivalent negative CO'' ion for which there is absolutely no justification or evidence; besides, the co-ordination value for the nickel atom is reduced to three which is also unusual. A more satisfactory explanation on the basis of Rây's view can here be offered. It is well known that there are many co-ordination compounds in which inspite of the manifestation of the primary valency of the central atom, the compound as a whole is non-electrolyte. Instances of this type are furnished by trinitro-triammine cobalt $\left[CO \begin{matrix}(NH_3)_3\\(NO_2)_3\end{matrix}\right]$, tetrachloro-diammine platinum $\left[Pt \begin{matrix}Cl_4\\(NH_3)_2\end{matrix}\right]$, trithiocyanato triammine chromium $\left[Cr \begin{matrix}(SCN)_3\\(NH_3)_3\end{matrix}\right]$ trichloro-triammine iridium $\left[Ir \begin{matrix}Cl_3\\(NH_3)_3\end{matrix}\right]$ etc. In these the atoms or groups like Cl, NO_2, SCN, etc. satisfying the primary valencies of the central atom are linked to the latter by non-ionizable or co-valent bonds, and are situated along with the co-ordinatively bound molecules in the same primary sphere of the central atom. In exactly the same way one or two of the CO groups in the carbonyl compounds may be regarded as bound to the central atom by co-valent bonds satisfying the normal or principal valencies of the central atom. Thus if we assume that the metallic atoms in their carbonyl compounds exert their lowest possible normal valency *i.e.*, two in these cases, we can easily arrive at the following electronic configurations for them.

Substance.	Electrons in K_{11} to M_{22}	M_{23}	M_{33}	N_{11}	N_{21} N_{22}	Total electrons.
1. $Ni(CO)_4$	18	4	6		6	34
2. $Fe(CO)_5$	18	4	6	2	6	36
3. $Cr(CO)_6$	18	4	6		6	34

In the nickel and chromium carbonyls one of the CO groups is bound by co-valent bond, supplying one electron to the central atom and occupying one co-ordination position, and at the same time it gains one electron from the central atom by transfer. In iron carbonyl, one of the CO groups is bound by two co-valent bonds supplying two electrons to the iron atom. The other CO groups in all the compounds are co-ordinatively linked each forming one co-ordination bond and supplying two electrons to the central atom. Their effective atomic numbers thus become equal to 34, 36, and 34 respectively. In nickel carbonyl as in the diamagnetic perfect nickel complexes the four of M_{ss} electrons are coupled with four of N_s. In iron and chromium compounds the 6 M_{ss} electrons are coupled with those of N_s. The arrangements in the case of iron and nickel carbonyls are perfectly analogous to those for their ordinary perfect complexes. These arrangements become clearer still if we consider the electronic configuration for the carbonyl group itself. This is best represented by the scheme—



(1) (2)

So that, the group CO can furnish either two co-valent bonds, or one co-valent bond after gaining one electron by transfer (*cf.* configuration no. 1). It can also form one co-ordination bond with a central metallic atom (configuration no. 2 above). In the first case it completes its octet by forming co-valent bonds. In other words it can behave either as a bivalent acid radicle (1) or simply as a neutral molecule (2) occupying one or two co-ordination positions.

In this connection it may be pointed out that the associated complexes as defined by Rây may sometimes re-arrange their co-ordinating electrons in symmetrical pairs of 6, 6 or 4, 4 outside the main quantum group of the central atom as is exemplified in carbon, nitrogen and recently discovered optically active beryllium, boron, arsenic, aluminium, copper and zinc compounds (*cf.* Mills and Gotts, *J. Chem. Soc.*, 1926, **129**, 3121; Boeseken and Meulenhoff, *J.C.S. Abstr.*, 1924, **126**, *i.* 776; Rosenheim and Plato, *Ber.*, 1925, **58**, 2000; Wahl, *Ber.*, 1927, **60**, 399). The 4, 4 groups are arranged tetrahedrally and the 6, 6 groups octahedrally.

It is not difficult to make assumptions regarding the locations of these 4, 4 or 6, 6 groups.

It may not be out of place here to point out that the ordinary conductivity water is not a sufficiently sure standard for susceptibility measurements; and we had to further purify this water by fractional solidification till a constant mass deflection in the Curie balance was obtained.

Our best thanks are due to Prof. Dr. D. M. Bose for his keen interest and many helpful suggestions in the course of this investigation.

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P.S.—In a paper recently published in the *Phil. Mag.* (1928, 5, 1048) and received here since the communication of the present paper, Bose has further developed his theory on a theoretical basis in which he has assumed as Rây has already done that in the case of cobaltous and nickelous complexes the co-ordinating electrons lie outside the M-shell.

Chromium Powder in Organic Synthesis.

By Sachindra Nath Chakrabarty and Sikhibhusan Dutt.

In a recent paper by Roy and Dutt (this *Journal*, 1928, **5**, 108) aluminium powder has been successfully employed in a number of organic syntheses of the types already elaborated by Frankland, Ullmann, Fittig, Reformatski, Wislicenus and others, using metals like sodium, copper, silver, zinc and mercury. From the results of that investigation it was thought that the metal chromium (which has become very cheap now-a-days on account of its manufacture by the 'thermite' process, and) which has similar properties to aluminum both physical and chemical, would also lend itself to organic syntheses. This would be interesting in view of the fact that the metal chromium has not, up to this time, been employed in organic reactions. These expectations have been partially realised and the following results have been arrived at.

1. Metallic chromium behaves in a similar manner to aluminium in most of the reactions that have been studied, but the vigour of the reaction is somewhat less and consequently the yields of the products are somewhat lower.

2. Unlike aluminium, chromium does not react with organic bromine and iodine compounds.

3. The successful results with chromium have been obtained with organic chlorine compounds in which the chlorine atoms are rather loosely attached to the molecule.

4. Chromium when freshly powdered from lump is found to be more reactive than the powder which has stood for some time.

5. The activity of the powder which has stood for some time can be renovated to a certain extent by heating it to red-heat in a current of pure dry hydrogen.

6. Chromium cannot be used in Reformatski's and Gattermann's syntheses, nor as a neutral reducing agent.

In all the cases referred to in this paper chromium was powdered by human agency, and naturally the powder was not so fine as in the case of other metals. Hence probably if the powder had been more fine, the yields in the cases of successful reactions would have been greatly increased.

The following two tables summarise successful and unsuccessful attempts using metallic chromium in various types of organic syntheses.

TABLE I.

Successful Attempts.

Type of reaction.	Reacting materials.	Product.	Yield (%).
Zincke's	Benzylchloride and benzene	Diphenylmethane	42
Friedel-Crafts'	Benzalchloride ,, ,,	Triphenylmethane	19·5
,, ,,	Benzotrichloride ,, ,,	Triphenylchloromethane	17
,, ,,	Benzoylchloride ,, ,,	Benzophenone	9
,, ,,	,, ,, ,, ,,	Triphenylcarbinol	28
,, ,,	Benzoylchloride and benzoic acid	Benzoylbenzoic acid	22
,, ,,	Acetylchloride and benzene	Acetophenone	11
Ullmann's	Ethyl chloracetate and ethyl acetate	Ethyl succinate	10
,, ,,	Chloracetic acid and acetic acid	Succinic acid	6
,, ,,	o-Chlorobenzoic acid and aniline	Phenylanthranilic acid	87
,, ,,	o-Chlorobenzoic acid and ammonia	Anthranilic acid	85

TABLE II.

Unsuccessful Attempts.

Types of reaction.	Reacting materials.	Expected product.
Ullmann's	Bromobenzene	Diphenyl
,,	Iodobenzene	,,
Friedel-Crafts'	Bromobenzene and benzene	,,
,,	Iodobenzene and ,,	,,
Ullmann's	Bromobenzene and phenol	Diphenylether
,,	Chlorobenzene ,, ,,	,,
,,	Bromobenzene and aniline	Diphenylamine
,,	Carbon tetrachloride	Hexachlorethane
Reformatski's	Acetophenone and ethyl bromacetate	Phenylmethyl-β-hydroxy ethylpropionate
Friedel-Crafts'	Chloroform and benzene	Triphenylmethane
,, ,,	Carbon tetrachloride and benzene	Triphenylchloromethane
Ullmann's	Dinitrochlorobenzene	Tetranitrodiphenyl
Wislicenus'	β-Iodopropionic acid	Adipic acid
,,	Chloroacetic acid	Succinic acid
Goske's	Thiodiphenylamine	Carbazole
Neutral reduction	Nitrobenzene and ammonium chloride	Phenylhydroxylamine

Experimental.

Diphenylmethane from Benzylchloride and Benzene.

A mixture of benzene (30 g.), benzyl chloride (15 g.) and freshly powdered chromium (5 g.) was heated on the water-bath under reflux for about three hours, till the evolution of hydrogen chloride had ceased. The reaction product was treated with a very dilute solution of caustic soda and then extracted with ether. The ether and the excess of benzene were then distilled off and the residual oil fractionated under diminished pressure. The diphenylmethane distilled off as a pale yellow liquid with a pronounced orange smell at 101°/40 mm.

Triphenylmethane from Chloroform and Benzene.

This was prepared in a similar manner to the method already described by Roy and Dutt (*loc. cit.*) in the case of aluminium powder.

Triphenylchloromethane from Benzotrichloride and Benzene.

A mixture of benzotrichloride (9·7 g.), benzene (22 g.) and freshly powdered chromium (5 g.) was heated on the water-bath under reflux for about five hours. The mixture was then poured into a few c.c. of concentrated hydrochloric acid and shaken well. The benzene layer was then separated, washed with water, dried and then distilled, at first under ordinary pressure and then under reduced pressure. The triphenylchloromethane distilled over as a pale yellow oil which solidified in the receiver as pale yellow needles melting at 106°. It gave triphenylcarbinol on boiling with water.

Triphenylcarbinol from Benzoylchloride and Benzene.

This was prepared from benzoylchloride, benzene and chromium powder in a manner similar to the above. The substance crystallised from alcohol in pale yellow needles melting at 160°. The acetyl derivative which was prepared melted at 97°.

Benzophenone from Benzoylchloride and Benzene.

This was prepared in a similar manner to the above from the same ingredients, with the only difference that the theoretical quantity of benzene was taken. The substance crystallised from dilute alcohol in colourless prisms melting at 48°, and was identified to be benzophenone.

Benzoylbenzoic Acid from Benzoylchloride and Benzoic Acid.

Benzoylchloride (7 g.), benzoic acid (6 g.) and chromium powder (5 g.) were heated together at 160° for about six hours, *i.e.*, until the evolution of hydrogen chloride had ceased. The product was then treated with cold dilute hydrochloric acid and then distilled in steam to remove the excess of benzoic acid. The residue was filtered and extracted with dilute ammonium hydroxide. The ammoniacal extract on acidification gave a colourless precipitate which was crystallised from hot water in shining white plates, m.p. 94°, and was identified to be benzoylbenzoic acid.

Acetophenone from Acetylchloride and Benzene.

A mixture of benzene (15 g.), acetylchloride (20 g.) and chromium powder (6 g.) was heated on the water-bath under reflux for about three hours. The mixture was then poured into crushed ice and the supernatant layer of benzene separated. This was washed with dilute sodium hydroxide and water, dried and then distilled. The portion distilling between 180° and 200° was collected. Acetophenone came over as a colourless oil. The oxime melted at 59° and the phenylhydrazone at 105°.

Diethyl succinate from Ethyl chloracetate and Ethyl acetate.

Ethyl chloracetate (12·2 g.), ethyl acetate (8·8 g.), and powdered chromium (4 g.) were heated together under reflux for about 3 hours, at 120°-130°. The mixture was then filtered off from the unaltered chromium powder and fractionated at the ordinary pressure, the portion distilling between 200° and 215° being collected. This was redistilled and collected between 216° and 218°, and the distillate was identified to be diethyl succinate.

Succinic Acid from Chloracetic Acid and Acetic Acid.

Sodium chloracetate (11 g.), sodium acetate (8 g.) and chromium powder (4 g.) were heated together at 110°-120° for about nine hours. The reaction product was then treated with dilute hydrochloric acid and filtered off from the unreacted chromium powder. The aqueous liquid on extraction with ether gave a small quantity of a crystalline solid melting at 185°, which was identified to be succinic acid.

Phenylanthranilic Acid from o-Chlorobenzoic Acid and Aniline.

A mixture of *o*-chlorobenzoic acid (5 g.), aniline (20 g.) and chromium powder (4 g.) was heated under reflux on the sand-bath for about four hours. The dark coloured reaction product was poured into excess of dilute hydrochloric acid when a brown precipitate separated out. This was filtered off, washed with water and dilute acid and finally crystallised from alcohol with the addition of animal charcoal in fine colourless plates melting at 183°, and was identified to be phenylanthranilic acid. When heated with concentrated sulphuric acid and poured into water, the substance gave acridone as a yellow precipitate, which did not melt even at 300°.

Anthranilic Acid from o-Chlorobenzoic Acid and Ammonia.

A mixture of *o*-chlorobenzoic acid (2·5 g.) and chromium powder (4 g.) was heated in a tube at 100° and a current of dry ammonia passed over the mixture for about five hours. The product was then treated with dilute hydrochloric acid until the precipitate first formed completely redissolved. An excess of saturated sodium acetate was then added, when the anthranilic acid was precipitated in brown flocks which were crystallised from hot water with the addition of animal charcoal in almost colourless needles melting at 143°.

The details of unsuccessful attempts are omitted. Further work in this direction is in progress.

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Compounds of Hexamethylenetetramine with certain Salts of Silver and other Metals and the Influence of Anionic Volume on the Capacity for Association by the Central Positive Atom.

By Priyadaranjan Rây and Jyotirmoy Dasgupta.

As the result of a long series of investigations on the nature of auxiliary valencies, Ephraim has obtained some very interesting and important results. It has been observed that the capacity of a cation to associate with neutral molecules increases with the atomic or molecular volume of the anions and so far, that under certain circumstances the usually characteristic co-ordination value of six is overstepped (Ephraim, *Ber.*, 1918, **51**, 644 ; 1919, **52**, 957; 1920, **53**, 548; 1921, **54**, 973). This increased capacity of the cations to associate with natural molecules like water and ammonia with the increase in volume of the anions has been attributed by Ephraim to the existence of holes or empty spaces in the crystal lattice when the anion and cation forming the compound possess essentially different molecular volumes. These holes are then filled up by the neutral molecules and the crystal is thereby stabilised. Well developed, highly symmetrical forms of crystals of salts rich in water of crystallisation are quoted as instances in support of the above view.

On the other hand, Ephraim (*Ber.*, 1918, **51**, 706) found that in the ammoniacates of silver halides which in the maximum take up 3 molecules of ammonia per atom of silver, the relationship is reversed. The stability diminishes from chloride to iodide inspite of the iodide ions being larger than the chloride ion. Similar anomalous results have also been obtained in the case of silver salts such as chlorate, bromate, iodate, perchlorate, perbromate, periodate, permanganate, nitrite and nitrate. This anomaly has been explained by Ephraim assuming that the ammoniacal silver halides are polymarised compounds in which the ammonia is distributed partially between the cation and the anion. In order to make a close examination of the influence of the anionic volume upon the capacity of the silver ion to associate with neutral molecules, a number of compounds of

silver salts with the non-volatile neutral molecule hexamethylenetetramine have been prepared and studied. These form the subject matter of the present paper. The following compounds of hexamethylenetetramine with various silver salts have been prepared.

$3AgCN, B$; $2AgCNO, B$; $2AgCNS, B$; $AgClO_4, B$; Ag_2CrO_4, B ; $4Ag_2Cr_2O_7, 5B, 4H_2O$; $Ag_2MoO_4, 2B, 2H_2O$; $Ag_2WO_4, 2B, H_2O$; $2Ag_2SO_4, 3B, 6H_2O$; $4Ag_2SO_4, 5B, 13H_2O$; $Ag_2ScO_4, 2B, 12H_2O$; where $B=(CH_2)_6N_4$.

To this a number of others already described by previous workers may be added for the sake of comprehensive comparison:

$AgF, B, 3H_2O$; $4AgCl, B$; $3AgBr, B$; $2AgI, B$: $AgClO_3, B, H_2O$ and $Ag_2C_2O_4, B$ (Vannino and Sachs, *Arch. Pharm.*, 1913, **251**, 290); $4AgBr, B$ (Schwartz, *Chem. Zeit.*, **14**, 787); $AgNO_3, B$ (Delepine, *Comt. rend.*, 1894, **119**, 1211); $3AgNO_3, 2B$ (Pratesi, *Gazzetta*, 1884, **13**, 437); where $B=(CH_2)_6N_4$.

In the case of the halides the capacity of silver for association diminishes from flourine to chlorine—an anomaly already observed by Ephraim in their corresponding ammonium compounds. In all other cases the general regularity is maintained, that is, the increase in the anionic volume is accompanied with the increased capacity of association of neutral molecules by the cation silver. So the results of Ephraim's investigations about the influence of anionic volume upon the capacity of cation to manifest auxiliary valencies are supported to a great extent by the nature of the hexamine compounds studied in the present paper. As for the anomaly in the case of the silver fluoride noted above, which runs parallel with the corresponding ammoniacate, an explanation similar to that suggested by Ephraim for the ammonicates can be accepted.

In order to study the influence of cationic volume upon its capacity for association with neutral molecules, two compounds of copper and cadmium cyanide have been prepared. Their formulae are given below along with that of silver cyanide for comparison:

$3CuCN, 2B$; $3Cd(CN)_2, B$; $3AgCN, B$.

Now as the silver and cadmium ions have almost the same volume, the composition of their hexamine compounds is similar.

On the other hand copper with a smaller atomic volume possesses a higher degree of associating power as is to be expected.

The cadmium compound is not strictly comparable with cuprous and silver compounds as in it cadmium is present as a divalent cation.

Again unlike sulphate and selenate, silver tellurate does not form any compound with hexamine. Though according to Ephraim's rule the associating power of the silver atom in silver tellurate should have been developed to the maximum extent. This is very likely due to the condensation and extreme insolubility of silver tellurate. Similar explanation holds good also in the case of borate, iodate, phosphate, arsenite and arsenate of silver which fail to associate with hexamine molecules. Most of the salts whose hexamine compounds are described in this paper are insoluble in water; so also are their hexamine compounds. Hence their method of preparation is based on the principle of substitution. That is, the salts are dissolved in strong ammonia solution when they form soluble ammoniacates, then the solution is treated with a strong solution of hexamine and and the mixed solution is evaporated when the hexamine compound crystallises out with the loss of ammonia.

$$m\text{AgX}, n\text{NH}_3 + p(\text{CH}_2)_6\text{N}_4 = m\text{AgX}, p(\text{CH}_2)_6\text{N}_4 + n\text{NH}_3$$

where X is an acidic radical and m, n and p are integral numbers.

Experimental.

Silver Cyanide and Hexamine.—Freshly precipitated silver cyanide was dissolved in dil. ammonia by warming. The solution was filtered to remove any suspended impurities and to this an excess of a concentrated hexamine solution was added. The solution was concentrated by evaporating on water-bath. The fine precipitate formed was filtered, washed with cold water and finally with absolute alcohol and dried in a vacuum over sulphuric acid.

For analysis a weighed quantity of the substance was decomposed by evaporating with dil. sulphuric acid on the water-bath till no smell of formaldehyde and hydrocyanic acid was perceived. The silver was then precipitated from the solution as silver chloride and estimated as usual. Nitrogen was estimated by combustion. (Found: Ag, 59·3, 59·3 ; N, 17·86. $3\text{AgCN},(\text{CH}_2)_6\text{N}_4$ requires Ag, 59·9 ; N, 18·0 per cent.).

It is a white crystalline silky substance insoluble in cold water. When warmed with water the filtrate gives test for hexamine indicating partial decomposition.

Silver Thiocyanate and Hexamine.—Freshly precipitated silver thiocyanate was dissolved in concentrated ammonia solution with the aid of a little heat. The solution was filtered and to this was added a concentrated solution of hexamine in excess. The solution was concentrated on water-bath and was then cooled when a white crystalline precipitate separated out. These crystals were collected and recrystallised from ammonia. The crystallised salt was filtered, washed and dried as in the previous case.

For analysis a weighed quantity of the substance was taken in a beaker and was covered with water. Then bromine water was added in excess. The sulphur was oxidised to sulphuric acid and silver changed into silver bromide. To the mixture was added about 10 c. c. of dilute nitric acid, and it was kept for sometime on the water-bath to remove the excess of bromine. The precipitated silver bromide was estimated in the usual way. Sulphur was estimated in the filtrate as $BaSO_4$. (Found: Ag, 46·16, 46·3 ; S, 13·5 ; N, 17·3. $2AgCNS, (CH_2)_6N_4$ requires Ag, 45·8 ; N, 17·8, S, 13·5 per cent).

Cuprous Cyanide and Hexamine.—The method of preparation is identical with those of the previous compounds.

A weighed quantity of the substance was taken and evaporated with dil. sulphuric acid till no smell of formaldehyde was perceived. To this was then added a concentrated solution of caustic soda and the whole kept on a boiling water-bath to dehydrate the copper oxide and at the same time to drive off all the ammonia formed from the hexamine by previous decomposition by the acid. The contents of the basin were cooled and the copper estimated as copper oxide. (Found: Cu, 35·0 ; N, 28·1. $3CuCN, 2(CH_2)_6N_4$ requires Cu, 34·6 ; N, 28·16 per cent.).

It is a white crystalline substance insoluble in water.

Cadmium Cyanide and Hexamine.—Freshly precipitated cadmium cyanide was dissolved in slight excess of dil. ammonia and to this a large excess of concentrated hexamine solution was added. The solution was filtered and evaporated on water-bath. The precipitate contained sufficient ammonia as ammoniacal compound. The precipitate was filtered, washed and suspended in a concentrated solution of hexamine and digested on the water-bath till the last trace of

ammonia had been removed. The white crystalline substance was filtered, washed and dried as usual. (Found: Cd, 52·7, 52·6; N, 22·4. $3Cd(CN)_2$, $(CH_2)_6N_4$ requires Cd, 53·1; N, 22·1 per cent.).

Cadmium was estimated as sulphate by evaporating with sulphuric acid.

Silver Cyanate and Hexamine.—Freshly precipitated silver cyanate dissolved in the smallest quantity of concentrated ammonia solution was added to a concentrated solution of hexamine in excess. The solution was filtered and allowed to evaporate spontaneously at the ordinary temperature. The fine crystalline precipitate obtained was recrystallised from ammonia in the cold, filtered, washed and dried in the usual way. (Found: Ag, 49·4; N, 19·07. $2AgCNO$, $(CH_2)_6N_4$ requires Ag, 49·1; N, 19·09 per cent.).

Silver Chromate and Hexamine.—Freshly precipitated silver chromate was dissolved in slight excess of dilute ammonia. The solution was filtered and crystallised with the addition of excess of hexamine solution at a comparatively low temperature on the water-bath when beautiful yellow crystalline crust separated. This was filtered and recrystallised from ammonia solution. The crystals were filtered, washed and dried as usual.

The yellow compound was also obtained by digesting the dark red silver chromate with a solution of hexamine. (Found: Ag, 45·63; N, 12·1, 12·3; Cr, 11·27. Ag_2CrO_4, $(CH_2)_6N_4$ requires Ag, 45·7; Cr, 11·0; N, 11·8 per cent.).

Silver Dichromate and Hexamine.—The freshly precipitated silver dichromate was dissolved in nitric acid with the aid of a little heat. The content was cooled and filtered. A concentrated solution of hexamine was added to this solution drop by drop. The beautiful orange-red crystals formed were separated, washed and dried as usual. (Found: Ag, 34·8; Cr, 16·7, 16·6; N, 11·2. $4Ag_2Cr_2O_7$, $5(CH_2)_6N_4$, $4H_2O$ requires Ag, 34·4; N, 11·2; Cr, 16·6 per cent.).

Silver Molybdate and Hexamine.—Freshly precipitated silver molybdate was dissolved in slight excess of concentrated ammonia. Then a concentrated solution of hexamine was added in excess. The solution was filtered and allowed to evaporate spontaneously in the dark when large, long, white shining crystals separated.

These were recrystallised from ammonia at the ordinary temperature and filtered, washed and dried in the usual way. (Found : Ag, 30·7 ; Mo, 13·66 ; N, 16·0. Ag_2MoO_4, $2(CH_2)_6N_4$, $2H_2O$ requires Ag, 31·1 ; Mo, 13·8; N, 16·17 per cent.).

Silver Tungstate and Hexamine.—The preparation is exactly similar to that of the molybdate compound.

Tungsten was estimated as WO_3 by repeated evaporation with strong nitric acid. Silver was estimated in the filtrate from tungstic acid. (Found: Ag, 27·73, 27·8; W, 23·3; N, 14·2. Ag_2WO_4, $2(CH_2)_6N_4$, $2H_2O$ requires Ag, 27·7 ; W, 23·57; N, 14·3 per cent.).

It is a white crystalline substance sparingly soluble in water. When boiled with water the substance is reduced ; when boiled with dil. nitric or sulphuric acid it is decomposed with the separation of tungstic acid accompanied by the liberation of formaldehyde.

Silver Sulphate and Hexamine.—(*a*) A solution of silver sulphate was gradually added to an excess of hexamine solution. The white crystalline precipitate was filtered, washed with a very dilute hexamine solution and finally with alcohol. It was then dried as usual. (Found: Ag, 37·9; N, 14·3. $2Ag_2SO_4$, $3(CH_2)_6N_4$, $6H_2O$ requires Ag, 37·5; N, 14·6 per cent.).

(*b*) On the other hand when a solution of hexamine was added to an excess of silver sulphate solution a different product was obtained. The substance was filtered, recrystallised from ammonia, washed with cold water and finally with alcohol and then dried as usual. (Found: Ag, 39·8, 40·0; N, 12·6. $4Ag_2SO_4$, $5(CH_2)_6N_4$, $13H_2O$ requires Ag, 39·6; N, 12·8 per cent.).

Silver Selenate and Hexamine.—The freshly precipitated silver selenate was dissolved in slight excess of ammonia. This was filtered and a concentrated solution of hexamine was added in excess. The solution was crystallised at ordinary temperature and the white crystals obtained were recrystallised from ammonia solution at room temperature. The crystals were finally washed and dried as usual. (Found: Ag, 25·4, 25·3; N, 13·15. Ag_2SeO_4, $2(CH_2)_6N_4$, $12H_2O$ requires Ag, 25·2; N, 13·1 per cent.).

Silver Perchlorate and Hexamine.—A solution of perchloric acid was neutrallised with freshly precipitated silver oxide by heating on water-bath. It was cooled filtered and to this a strong solution of

hexamine was gradually added. The white precipitate obtained was recrystallised from ammonia, filtered, washed, with cold water and finally with alcohol and dried in the usual way. (Found: Ag, 31·0, 31·3; N, 16·4. $AgClO_4$, $(CH_2)_6N_4$ requires Ag, 31·1; N, 16·1 per cent.).

General Properties of the Compounds.—All these substances are more or less easily soluble in ammonia solution. They are decomposed by mineral acids on warming with evolution of formaldehyde. Caustic alkalis decompose them with the formation of the metallic oxide. On being heated in a dry test tube they decompose with charring and emitting a fishy odour characteristic of amines.

A hexamine compound of cuproso-cupric cyanide of uncertain composition was obtained when cuprous cyanide was dissolved in concentrated ammonia and a current of air passed through it for several hours after the addition of hexamine solution. At first an ammonium compound of cupric cyanide separated then a brown precipitate began to be formed, when the liquid was filtered and more air passed through. The precipitate was a brown crystalline substance. It decomposes at ordinary temperature giving smell of cyanogen gas when kept for any length of time.

Silver benzoate gave a precipitate when evaporated spontaneously from ammoniacal solution to which hexamine was added in excess. The substance even after recrystallisation from ammonia did not give constant results.

Silver sulphite and silver salicylate behaved like the benzoate. They were all well-defined crystalline substances insoluble in water. The silver sulphite compound was found to be very unstable even at the ordinary temperature.

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Complex Compounds of Gold with Mercaptanic Radicles. Part II. Residual Affinities of Chlorauric Acid.

By Prafulla Chandra Rây and Kshitish Chandra Bose-Rây.

It has been shown in Part I (*J. Indian Chem. Soc.*, 1924, **1**, 36) that gold chloride or rather chlorauric acid reacts with ethylene dithioglycol, triethylene trisulphide and benzalethylene sulphide forming compounds in which the valency of gold varies from 2 to 5. The study has now been extended to 1:4-dithian as also to triethylene tetrasulphide.

These sulphides react with gold chloride yielding:—

(*a*) $HAu_2Cl_3(C_2H_4S)_2$ *i.e.*, $2AuCl.HCl.(C_2H_4S)_2$;

(*b*) $AuCl,\ (C_2H_4S)_2$;

(*c*) $2(H)\ AuCl_4,\ 3(C_2H_4S)_2,\ 4H_2O$;

(*d*) $KAuCl_4,\ 3[(C_2H_4S)_2],\ 4H_2O$;

(*e*) $(H)\ KAuCl_5,\ 3[(C_2H_4S)_2],\ 2H_2O$;

(*f*) $AuCl(C_2H_4)_3S_2$

Indirectly we have also a proof that when associated with metallic chlorides, the dithian is converted into triethylene trisulphide ; in other words the group C_2H_4S polymerises (*cf. J. Indian Chem. Soc.*, 1926, **3**, 73).

The reason why in (*c*), the hydrogen atom has been placed under bracket is that it is really a derivative of chlorauric acid having the empirical formula $2[HCl,AuCl_3],\ 3(C_2H_4S)_2,\ 4H_2O$, since on neutralising its aqueous solution with potassium carbonate it effervesces and the neutral solution on evaporation yields the corresponding salt *viz.*, $KAuCl_4,\ 3(C_2H_4S)_2,\ 4H_2O$. One notable feature is that if exactly the theoretical quantity, *i.e.*, half a molecule of potassium carbonate be taken for neutralisation only the salt

(*e*) is obtained. If, on the other hand, one molecule of potassium carbonate be used for neutralisation, two successive crops are obtained, the first conforming to (*e*), *i.e.*, $KAuCl_4$, HCl, $3[(C_2H_4S)_2]$, $2H_2O$,* whereas the second to (*d*), *i.e.*, $KAuCl_4$. $3[(C_2H_4S)_2]$, $4H_2O$. Cryoscopic determination of the molecular weight of (*c*) proves that there are altogether four ions in the compound.

Another noteworthy feature is the dropping off from triethylene trisulphide and tetrasulphide of one or more atoms of sulphur as the case may be. Thus in the latter 2 atoms of sulphur are parted with as in the compound AuCl. $(C_2H_4)_3S_2$. The sulphur, in these cases, has been found to undergo oxidation to sulphuric acid (*cf.* Rây and Bose-Rây, *J. Chem. Soc.*, 1922, **121**, 1279 ; Mann and Pope, *ibid*, 1923, **123**, 1179).

The action of ammonia and organic bases on these compounds has been found to be noteworthy. Thus by the action of ammonia upon (*a*) two compounds having the formula Au_3Cl_2. $6(NH_3)$ and $AuCl.NH_3$ respectively have been obtained. As the former explosive derivative is insoluble in all the ordinary solvents, no definite light could be thrown on its structure by recourse to physical methods. By the action of ammonia upon (*c*) in aqueous solution a compound having the composition, $Au(NH_3)_2$. $1\frac{1}{2}H_2O$ was obtained. This was also found to be explosive. These are evidently of the nature of fulminating gold compounds investigated by Raschig and others (*Annalen*, 1886, **235**, 355).

Pyridine however acting upon (*a*) produced the compound Au_2Cl_2. $\frac{1}{2}[(C_2H_4S)_2]$. C_5H_5N. One chlorine atom and half the dithian molecule are removed and their place is taken up by a molecule of pyridine. Often complete removal of the dithian molecule takes place, as for instance, when the compound (*b*) is treated with pyridine, the sulphide is entirely substituted for a pyridine molecule.

Under slightly modified condition (*vide* Experimental) the product had the empirical composition, 2AuCl, $(C_2H_4S)_2$. As it was insoluble in ordinary solvents its molecular weight could not be determined.

* The compound is really a derivative of 2HCl, $AuCl_3$. A corresponding compound of $FeCl_3$ with quinidine *i.e.*, 2HCl. $FeCl_3$. $C_{20}H_{24}N_2O_2$ is known (Scholtz, *Ber. Deut. Pharm. Ges.*, **18**, 48.)

When however (*c*) is similarly treated, we get $AuCl_3 . C_5H_5N$. Here the sulphide complex is replaced by a molecule of the base.

It thus appears that there is a close family likeness between the complex gold compounds (studied in this paper) and similar platinum compounds, so far as their action towards ammonia and organic bases is concerned. The "*thio*" constituents of some of these gold compounds like those of platinum, are partially or completely replaced by the base (Rây, Guha and Bose-Rây, *J. Indian Chem. Soc.*, 1926, **3**, 358 ; Rây, Bose-Rây and Adhikari, *J. Indian Chem. Soc.*, 1927, **4**, 467).

Experimental.

Preparation of $HAu_2Cl_3 (C_2H_4S)_2$ *and* 2 (H) $AuCl_4$, $3(C_2H_4S)_2$ $4H_2O$.

An excess of an aqueous solution of gold chloride was added to dithian and the mixture occasionally stirred. After about 18 hours the orange precipitate was washed successively with water, alcohol, ether and benzene till the filtrate was no longer coloured. The mass was finally washed with ether and dried in a vacuum. (Found : Au, 63·49 ; Cl, 17·22. HAu_2Cl_3, $(C_2H_4S)_2$ requires Au, 63·49 ; Cl, 17·16 per cent.).

The filtrate on spontaneous evaporation in a vacuum desiccator, deposited shining orange yellow crystals. (Found : Au, 35·07 ; Cl, 25·53. $2HAuCl_4$, $3(C_2H_4S)_2$, $4H_2O$ requires Au, 35·5 ; Cl, 25·58 per cent). Both the above substances were found to contain dithian.

Ionisability of the Compound $2HAuCl_4$, $3(C_2H_4S)_2$. $4H_2O$

Observation.	Dilution (mols. per litre.)	Depression of F. P.	No. of ions (assuming complete ionisation).
I	0·08597 M	0·47°	3
II	0·03272 M	0·22°	3·6

The number of ions present at infinite dilution is therefore taken to be four.

Action of Ammonia upon HAu_2Cl_3, $(C_2H_4S)_2$.

Ammonia gas was passed through a suspension of the complex sulphide in water for about half an hour. The insoluble brown precipitate was collected, washed with water, alcohol, benzene and

ether and dried. It could not be crystallised, since it was practically insoluble in common media. It has no m. p. but explodes on heating. (Found: Au, 85·21 ; Cl, 6·10 ; N, 7·01. Au_5Cl_2, $6(NH_3)$ requires Au, 85·06 ; Cl, 6·13 ; N, 7·25 per cent.). The preparation was repeated several times with identical results.

The filtrate on evaporation in a vacuum gave a crop of white crystals which were washed with water, alcohol and ether and dried. (Found: Au, 78·81 ; Cl, 14·14 ; N, 5·86. AuCl, NH_3 requires Au, 78·96 ; Cl, 14·22 ; N, 5·61 per cent. Sulphur was found to be absent.).

Action of Pyridine upon $HAu_2Cl_3(C_2H_4S)_2$.

The substance, $HAu_2Cl_3(C_2H_4S)_2$ was digested with pyridine for 15 minutes on a water-bath, when it completely went into solution. The solution was filtered and left aside when gradually a crop of white crystals separated. This was washed with a little pyridine, and dried by pressing between folds of filter paper and kept in a vacuum over sulphuric acid. The substance is very sensitive to light and is reduced when exposed to sun-light. It had no m. p. (Found: Au, 65·2, 65·31 ; Cl, 11·61, 11·43 ; N, 2·91. $4AuCl$, $(C_2H_4S)_2$, $2C_5H_5N$ requires Au, 65·23 ; Cl, 11·75 ; N, 2·32 per cent.). The substance was found to contain dithian.

Action of Benzylamine upon $HAu_2Cl_3(C_2H_4S)_3$.

On adding an excess of benzylamine to the substance much heat was generated. The mixture was heated on a water-bath for 15 minutes and cooled. The semi-solid mass thus obtained had a dark appearance due to portion having undergone reduction. It was extracted with absolute alcohol. Ether was then added to the filtered extract which caused precipitation of a white crystalline substance. It was washed with water to free it from benzylamine hydrochloride and dried in an amber-coloured desiccator. (Found: Au, 59·07 ; Cl, 10·00. AuCl $(C_7H_7NH_2)$ requires Au, 58·31 ; Cl, 10·40 per cent.). Sulphur was found to be absent.

Preparation of AuCl $(C_2H_4S)_2$.

A mixture of dithian and an excess of an aqueous solution of gold chloride was heated on a water-bath with occasional shaking for 3-4 hours. The insoluble mass was then filtered off, washed with water, alcohol, and ether, and was extracted with hot benzene to

remove the unacted upon dithian. The residue thus purified was a pale yellow precipitate. (Found: Au, 55·31 ; Cl, 10·58 ; $AuCl(C_2H_4S)_2$ requires Au, 55·88 ; Cl, 10·00 per cent. Sulphur was found to be present.)

The aqueous filtrate deposited, on being long kept in a vacuum, orange yellow shining crystals which were identical with those previously obtained (*vide* p. 547) and had the composition $2HAuCl_4$, $3(C_2H_4S)_2$, $4\ H_2O$. It will thus be seen that chlorauric acid undergoes reduction in the previous case.

Action of Pyridine upon $AuCl\ (C_2H_4S)_2$.

(*a*) The compound, $AuCl(C_2H_4S)_2$ was kept suspended in pyridine in a dark place for half an hour. During this period, the pale yellow gold compound was gradually converted into a white substance. This was washed with pyridine, alcohol and ether and dried in an amber-coloured desiccator. (Found: Au, 62·88 ; Cl, 12·27. $AuCl,C_5H_5N$ requires Au, 63·24 ; Cl, 11·4 per cent.). Sulphur was found to be absent. If the reaction is carried on in presence of light reduction takes place.

(*b*) $AuCl\ (C_2H_4S)_2$ was heated with an excess of pyridine to 60-70° until everything went into solution. The solution was filtered, cooled and diluted with ether when a white crystalline deposit was obtained. This was washed with alcohol and ether to remove pyridine and dried in a desiccator. (Found: Au, 67·44; Cl, 11·87; S, 10·07. $2[AuCl],\ (C_2H_4S)_2$ requires Au, 67·31; Cl, 12·13; S, 10·94 per cent.). Nitrogen was found to be absent.

Preparation of $KAuCl_4,\ 3\ [(C_2H_4S)_2],\ 4H_2O$.

To the aqueous solution of $2[HAuCl_4],\ 3(C_2H_4S)_2,\ 4H_2O$ molar quantity of potassium carbonate was added, carbon dioxide escaped with effervescence and the solution on concentration in a vacuum over sulphuric acid yielded yellow crystals which conform to the formula given above. (Found: Au, 24·36; Cl, 16·94; K, 5·23; S, 23·24. $KAuCl_4,\ 3[(C_2H_4S)_2],\ 4H_2O$ requires Au, 24·33; Cl, 17·53; K, 4·82; S, 23·70 per cent.).

Preparation of $HCl,\ KAuCl_4,\ 3(C_2H_4S)_2,\ 2H_2O$.

If however in the above preparation instead of adding potassium carbonate in the molar proportion an equivalent quantity *i.e.*, $\frac{1}{2}K_2CO_3$ be used we get the compound (H) $KAuCl_5,\ 3(C_2H_4S)_2$,

$2H_2O$ in the shape of yellow crystals. (Found: Au, 23·94, 23·99, 24·03; K, 5·11; Cl, 21·78; S, 23·42. (H) $KAuCl_5$, $3(C_2H_4S)_2$, $2H_2O$ requires Au, 24·30 ; K, 4·94; Cl, 21·81; S, 23·72 per cent.).

It should be noticed that the molecular weight of (*d*) and (*e*) are almost the same, namely 810 and 809·5 respectively; hence the percentage of Au, K, and S come out almost the same, but the difference in the percentage of chlorine is marked. As the quantity of potassium carbonate used is half that of the previous compound an acid salt is evidently formed.

From the mother-liquor of (H)$KAuCl_5$, $3(C_2H_4S)_2$, $2H_2O$ potassium chloraurate, $KAuCl_4$, $5H_2O$ is obtained. (Found: Au, 42·74; K, 7·90; Cl, 30·07; S absent. $KAuCl_4$, $5H_2O$ requires Au, 42·09; Cl, 30·34; K, 8·33 per cent.).

Preparation of $AuCl(C_2H_4)_3S_2$.

Triethylene tetrasulphide (m.p. 104°, *J. Chem. Soc.*, 1920, **117**, 1090) and an excess of gold chloride in water were heated on a water-bath for 7 to 8 hours with occasional shaking, when a brick-red mass was obtained. This was collected, washed with water alcohol and hot benzene to remove the uncondensed parent bodies and finally dried in a desiccator. (Found: Au, 52·03; Cl, 9·33; S, 16·82. $AuCl(C_2H_4)_3S_2$ requires Au, 52·67; Cl, 9·38; S, 18·19 per cent.).

Action of Ammonia upon $2(H)AuCl_4$, $3(C_2H_4S)_2$, $4H_2O$.

Ammonia gas was passed through an aqueous solution of this compound, when a brown precipitate was thrown down. This was washed with water, alcohol, ether and benzene. It was found to be highly explosive and conformed to the formula, $Au(NH_3)_2$, $1\frac{1}{2}H_2O$. (Found: Au, 75·84; N, 10·14. $Au(NH_3)_2.1\frac{1}{2}H_2O$ requires Au, 76·36; N, 10·85 per cent.). Both sulphur and chlorine were found to be absent.

Action of Pyridine upon $2[HAuCl_4]$, $3(C_2H_4S)_2$, $4H_2O$.

(*a*) The gold compound was digested with pyridine on a water-bath for 15 minutes when a portion went into solution leaving a mass of white crystals. The white crystals were further purified by crystallisation from water and on analysis proved to be the sulphone of dithian. Evidently the chlorine atoms set free in the reaction, acted as oxidising agent. (Found: S, 35·80; C, 25·52; H, 4·55. $C_4H_8O_4S_2$ requires S, 34·78; C, 26·09; H, 4·35 per cent.).

The solution on cooling deposited a crop of orange crystals. This was washed with water and dried in a vacuum desiccator. It had no m.p. but charred at about 210°. (Found: Au, 46·15; Cl, 25·97; N, 4·40; C, 21·70; H, 2·15. $AuCl_3$, $1\frac{1}{2}C_5H_5N$ requires Au, 66·68; Cl, 25·12; N, 4·91; C, 21·33; H, 1·8 per cent.).

The mother-liquor, on spontaneous evaporation, yielded a crop of light orange crystals, which were washed with water and dried in a vacuum. (Found: Au, 42·72; Cl, 22·89. $AuCl_3$, $2C_5H_5N$ requires Au, 42·70; Cl, 23·07 per cent.). Sulphur was proved to be absent.

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Cf. foot note, p. 5.

Dyes derived from Quinoline-2-aldehyde.

By Amarendra Nath Dey and Sikhibhushan Dutt.

Triphenylmethane dyestuffs belonging to the malachite green series have been obtained by condensing alkyl or ary substituted anilines with various aldehydes including a few heterocyclic aldehydes like furfurol. Most of them are of little theoretical importance apart from the fact that being similar in constitution to malachite green, they have analogous properties.

In connection with the effect of a heterocyclic nitrogen atom on colour which has been the subject of a number of communications from this laboratory (*cf.* Tewari and Dutt, this *Journal*, 1926, **3**, 161 ; 1927, **4**, 201 ; 1928, **5**, 108), it was thought advisable to try it in the triphenylmethane dyestuffs as has already been tried in the pyronine series. For this purpose the most useful compound to start with would be α-pyridine aldehyde, which on condensation with substituted anilines would give a series of colouring matters strictly comparable to the corresponding dyestuffs obtained from benzaldehyde. Unfortunately α-pyridine aldehyde is such an exceedingly difficult compound to get at that for all intents and purposes its employment in the preparation of dyestuffs is an impracticable affair. Consequently attention was directed to quinoline aldehyde which has been recently prepared and described by Hammick (*J. Chem. Soc.*, 1923, **123**, 2882 ; 1926, **129**, 1302). The malachite green series of dyestuffs thus derived from quinoline aldehyde would be strictly comparable to the corresponding dyestuffs obtained from naphthalene aldehyde.

Apart from that consideration it would also be interesting to see whether such dyes which contain a quinoline nucleus have got photosensitising properties just in the same way as cyanine or pinacyanol which has also got a quinoline nucleus in the molecule.

Quinoline-2-aldehyde condenses very easily with mono- or di-substituted anilines in presence of concentrated hydrochloric

acid or zinc chloride with formation of colourless leuco compounds, which can be oxidised to the colouring matter by means of manganese dioxide or lead peroxide. The colouring matters can also be prepared direct without the intermediate formation of leuco compounds by heating quinaldine-tribromide (Hammick, *loc. cit.*) with substituted anilines in presence of zinc chloride or zinc oxide or without any condensing agent at all. The dyestuffs thus obtained are all green or bluish green in colour, very stable toward light and are practically devoid of all photo-sensitising properties.

The following substituted anilines have been condensed with quinoline aldehyde and the corresponding dyestuff obtained: dimethylaniline, diethylaniline, methylbenzylaniline and ethylbenzylaniline.

Experimental.

Tribromoquinaldine.—This was prepared according to the method given by Hammick (*J. Chem. Soc.*, 1923, **123**, 2882).

Quinoline-2-aldehyde was prepared from the above by the method recommended by Hammick (*loc. cit.*).

Condensation of Quinoline-2-aldehyde and Dimethylaniline.—Quinoline-2-aldehyde (5 g.), dimethyl-aniline (10 g.) and zinc chloride (2 g.) were mixed together and heated for about three hours on water-bath. The excess of dimethylaniline was then removed by steam distillation. The solid residue was dissolved in hydrochloric acid and precipitated by a dilute solution of sodium carbonate. The dark brown leuco base obtained was dissolved in a 60 per cent. solution of acetic acid and treated with the requisite quantity of freshly prepared manganese dioxide and the whole mass left on water-bath for about 45 minutes. A deep violet coloured solution was obtained which was filtered and saturated with sodium acetate and left overnight. The precipitate dye was collected and dissolved in acetic acid and reprecipitated by a solution of sodium carbonate. The colour base thus obtained was crystallised from a mixture of chloroform and ligroin. It is dark bluish crystals, dissolves in water and in dilute acetic acid with a deep violet colour. In dilute mineral acid it shows a green colour. It also dissolves in alcohol and chloroform with a violet colour. It melts at

196°-198°. (Found: N, 10·3. $C_{26}H_{27}N_3O$ requires N, 10·5 per-cent.).

Condensation of Quinoline-2-aldehyde with Diethylaniline, Methylbenzylaniline and Ethylbenzylaniline.—In a similar way the above mentioned bases were condensed with quinoline-2-aldehyde. The colour bases obtained all dissolved in alcohol or chloroform with deep blue, greenish blue and green colour respectively and melted at 144°-145°, 172°-174° and 252°-254° respectively. [Found: N, 8·9 (Calc. N, 9·3 for $C_{30}H_3N_3O$). Found: N, 7·8 (Calc. N, 8·06 for $C_{36}H_3N_3O$). Found: N, 7·2 (Calc. N, 7·2 for $C_{38}H_{35}N_3O$)]. The colour bases combine with acetic acid and oxalic acid but the compounds thus obtained are not sufficiently stable and decompose easily into the colour base and the acid. The colour bases however dissolve in glacial acetic acid with violet, green-blue and blue colour respectively.

Condensation of Dimetheylaniline and w-Tribromoquinaldine.—Quinaldine tribromide (5 g.) and dimethylaniline (5 g.) were heated together on water-bath for about two hours. The excess of dimetheylaniline was removed by steam distillation and the residue dissolved in acetic acid and the dye and carbinol base obtained as mentioned above. The carbinol base obtained gave on analysis N=9·95 (calc. N, 10·5 per cent. for $C_{26}H_{27}N_3O$).

In this case the yield is better.

This method was also utilised to get the corresponding dyes from diethylaniline, methylbenzylaniline and ethylbenzylaniline. In the case of diethylaniline the heating was done for about half an hour only. Longer heating decomposes the carbinol base formed, the hydrobromic acid formed reducing it to the leucobase state.

It was therefore necessary to oxidise with a slight amount of freshly prepared manganese dioxide in all the cases mentioned above and thus get the substances as carbinol base completely.

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Adsorption of Ions by Sols of Aluminium Hydroxide and Vanadium Pentoxide.

By D. N. Chakravarti and N. R. Dhar.

In two recent communications (*Koll-Zeit.*, 1927, **43**, 377; 1928, **45**, 12) M. N. Chakravarti and N. R. Dhar have deduced an absorption equation based on Langmuir's conception of residual valency, and have shown that this equation agrees satisfactorily with all their experimental results. Moreover the values of adsorption calculated from this equation are in much better agreement with the experimental results than the absorptions calculated from Freundlich's equation.

From the equation it follows that when the amount of adsorption is high, bivalent and trivalent ions are less absorbed than an univalent ion. On the other hand, when the amount of adsorption is small bi- and tri-valent ions are adsorbed more than an univalent ion. In order to test the foregoing conclusions we have carried on experiments on the adsorption of electrolytes by sols of aluminium hydroxide and vanadium pentoxide prepared in the cold.

In the adsorption of electrolytes by a sol of aluminium hydroxide or by freshly precipitated aluminium hydroxide there is great divergence among the results of different investigators. The following results were obtained by Gann (*Koll. Chem. Beihefte*, 1916, **8**, 63) with a sol of aluminium hydroxide of concentration of 2 gms. of Al_2O_3 per litre.

Anions.	Coagulating power.	Adsorption in millimoles per gm. of Al_2O_3.
Salicylate	0·125	0·30
Picrate	0·250	0·18
Oxalate	2·770	0·18
Ferricyanide	10·000	0·09
Ferrocyanide	12·500	0·073

On the other hand the results obtained by Weiser and Middleton (*J. Phys. Chem.*, 1920, **24**, 630) are different from those of Gann and are as follows :—

Anions.	Coagulating power.	Adsorption in millimoles per gram of Al_2O_3.
Ferrocyanide	10·64	0·3202
Thiosulphate	5·32	0·4096
Ferricyanide	7·52	0·4046
Sulphate	3·75	0·4984
Oxalate	2·86	0·5710
Chromate	1·54	0·4352
Dithionate	1·23	0·3284
Dichromate	1·13	0·3185
Phosphate	2·89	0·8088

From the above results it is evident that in the majority of cases the greater the valency and hence the coagulating power of an ion and the less is its adsorption. It is evident from these results that aluminium hydroxide is a good adsorbent of different ions although Ishizaka has shown that grown alumina can adsorb ions only to the extent of 0·002 to 0·05 millimoles per gram of adsorbent. On the other hand Sen (*J. Phys. Chem.*, 1927, **31**, 686) has obtained the following results in the adsorption of acids by freshly precipitated aluminium hydroxide.

Acids. ...	... Citric.	Oxalic.	Tartaric.	Sulphuric.
Adsorption in millimoles ...	0·783	0·952	0·933	0·896

From the above results it will be seen that the precipitated aluminium hydroxide has a very high adsorptive power.

We have carried on experiments on the adsorption of anions by a sol of aluminium hydroxide prepared in the cold. The sol was prepared by the repeated washing of a precipitate of aluminium hydroxide prepared at the ordinary temperature by the action of aluminium nitrate and ammonium hydroxide. When the precipitate of aluminium hydroxide is practically free from electrolytes, it passed into a stable sol. The concentration of the sol was 2·42 gms. of Al_2O_3 per litre. 20 C.c. of the sol were taken in well washed and dried stoppered bottles and 5 c.c. of N/10 solutions of different electrolytes added and the volume made up to 50 c.c. in each case. It was kept overnight and the anions unadsorbed estimated in the clear supernatant liquid. With each ion two such bottles were arranged and from the mean the adsorption in millimoles per gram

of Al_2O_3 calculated. The following results were obtained:—

Anions.	Adsorption in millimoles per gram of Al_2O_3.
Bromate . . .	1·4600
Chloride . . .	1·3900
Iodate . . .	1·3520
Dichromate . . .	0·4964
Ferrocyanide . . .	0·3595
Oxalate . . .	0·1549

Thus we get the following order of adsorption, bromate being adsorbed the most and the oxalate the least:—

Bromate >Chloride>Iodate>Chromate>Ferrocyanide>Oxalate. It is also found that the bromate ion possesses the least coagulating power of all the other monovalent ions.

From the following results it will be seen that all the univalent ions, chloride, bromate, and iodate are all highly adsorbed and the adsorption is greater than the adsorption of bi- and poly-valent ions. The adsorption of dichromate is less than that of the tetravalent ferrocyanide ion. It is difficult to explain the low adsorption of oxalate ion by a sol of aluminium hydroxide. Our experimental results conclusively prove that in general the smaller the valency of an ion the greater is the adsorption by a sol of aluminium hydroxide. These experimental results on the sol of aluminium hydroxide support our conclusions expressed in previous papers (*J. Phys. Chem.*, 1924, **28**, 457; 1926, **30**, 628; 1927, **31**, 997) that in general an ion which has a small valency and coagulating power for a colloid is most adsorbed by the colloid in question.

It will be observed from the foregoing tables that the adsorption of an ion by the sol, with which we made experiments, is appreciably greater than the adsorption obtained by Gann, and Weiser and Middleton. This difference is certainly due to the following reasons:—It has been repeatedly observed that the adsorptive power and chemical reactivity of a substance become less when the substance is heated. Weiser and Middleton prepared their sol of aluminium hydroxide in boiling water, consequently the sol became aged and lost chemical reactivity and the power of adsorption appreciably. Our sol was not heated at all. It was prepared in the cold and washsd also with cold water and consequently it did not age and did not lose its chemical reactivity and the adsorptive power of our sol was greater than those prepared by the workers. From the resuls of Sen it will be seen that he

obtained very high adsorption with freshly precipitated aluminium hydroxide. This is mainly due to the fact that Sen prepared his aluminium hydroxide in the cold. Moreover M. N. Chakravarti and N. R. Dhar (*loc. cit.*) obtained the fairly high adsorption of anions with a freshly precipitated sample of aluminium hydroxide prepared in the cold.

Adsorption experiments were also carried on with vanadium pentoxide sol, which was prepared according to the method of Biltz. Three grams of ammonium vanadate were made into a paste with water and 22 c. c. of 10 per cent. HCl added. A red precipitate of vanadium pentoxide is formed. The precipitate was freed from the mother-liquor by continual washing, and when free from ammonium chloride and added HCl, it begins to pass into the colloidal state. On adding 500 c. c. of water to the precipitate it passad into a red colloid, which was dialysed for eight days till the outside water was free from electrolytes.

The sol was estimated by evaporating to dryness on a platinum crucible over water-bath and then igniting and weighing it as V_2O_5. It contained 1·41 grams of V_2O_5 per litre. This sol was found to be negatively charged.

On coagulating the sol with different electrolytes a major portion of the sol was precipitated and only a small portion remained in solution which was estimated in each case by reducing it with sulphurous acid and titrating the vanadyl salt thus produced with standard potassium permanganate.

20 C. c. of the sol were taken in stoppered bottles and 5 c. c. of M/10 solutions of different electrolytes added. The volume was made up to 50 c. c. in each case. The filtrate was evaporated to dryness in a platinum crucible over water-bath and weighed.

The following results were obtained :—

Electrolytes.	Total original before adsorption in 50 c. c. of the mixture.	Total adsorption in 50 c. c. and V_2O_5.	Amount of V_2O_5 in 50 c. c.	Adsorption in 50 c. c.	Gram mole adsorbed per gm. of V_2O_5.
KCl (estimated as K_2SO_4).	0·0845	0·07225	0·0075	0·01975	0·00804
$BaCl_2$ (estimated as $BaSO_4$).	0·2320	0·2275	0·0056	0·0101	0·00153
$Al(NO_3)_3$ (estimated as Al_2O_3).	0·0505	0·05875	0·0135	0·00525	0·00364
$Th(NO_3)_4$ (estimated as ThO_2).	0·3380	0·31075	Nil.	0·02735	0·00368

When vanadium pentoxide sol was precipitated with $Th(NO_3)_4$ it sets to a stiff jelly and hence the determination of the amount of adsorption has to be carried on with great difficulty. From the above results it will be seen that the univalent potassium ion is more adsorbed than the bivalent or polyvalent ions. There is some uncertainty regarding the adsorption of aluminium and thorium salts because of the marked hydrolysis of these substances.

It is also very interesting to note in this connection that the amount of vanadic acid remaining in solution after precipitation of the colloidal portion is greatest when coagulated with aluminium nitrate, and then comes KCl, and then barium chloride and finally thorium nitrate in which case no trace of vanadic acid could be detected in the filtrate. It appears that thorium vanadate is very sparingly soluble.

Summary.

(1) The adsorptions of bromate, chloride, iodate, dichromate, ferrocyanide and oxalate ions by a sol of aluminium hydroxide prepared in the cold have been determined.

(2) The adsorptions of potassium, barium, aluminium and thorium ions by a dialysed sol of vanadium pentoxide have been measured.

(3) The experimental results show that an univalent ion is adsorbed more than a bivalent and a trivalent ion with both these sols.

(4) These results are in agreement with the deductions from the adsorption equation of the authors.

CHEMICAL LABORATORIES OF THE ALLAHABAD UNIVERSITY AND VICTORIA COLLEGE OF SCIENCE, NAGPUR.

Received July 12, 1928.

The Solubility of Mercuric Bromide in Ethyl and Methyl Alcohols.

By K. L. Malhotra.

In the course of another piece of work (Dunnicliff and Lal, *Analyst*, 1927, **52**, 329) it was considered necessary to determine the solubility of mercuric bromide in (*a*) wet alcohol and (*b*) " absolute " alcohol of a purity such as would be easily attainable. This work was done some time ago (Indian Science Congress, Calcutta, 1928) but in view of the solubility tables given by Lloyd and collaborators (*J. Chem. Soc.*, 1928, **133**, 658) it was thought that these values might be of use to other workers.

Experimental.

The recrystallised mercuric bromide (m. p. 242-243°) gave a degree of purity 99·76%.

The alcohols were dried first by standing over anhydrous potassium carbonate and then by repeated redistillation over freshly burnt lime. $D_{4^\circ}^{18^\circ}$=0·7943 corresponded to 99·78 per cent. ethyl alcohol and that of methyl alcohol=0·7961 corresponded to 99·88 per cent. alcohol by weight.

The determination of solubility.—Unless otherwise mentioned the solubility determinations were made by Alexeev's synthetic method (*Bull. Soc. Chim.*, 1880, (*ii*), **38**, 145) in a thermostat controlled electrically to within ± ·05°.

Solubility in 99·78 *per cent Ethyl Alcohol.*

Weight of mercuric bromide in gms.	Weight of alcohol in gms.	Temp. °C.	Solubility in 100 gms. of alcohol.
0·8882	3·6949	0·0	24·04*
0·4158	1·5804	16·15	26·25
1·1552	4·0678	24·95	28·40†
1·4800	5·0542	29·15	29·28†
0·4690	1·5375	31·35	30·05
0·4939	1·5832	34·30	31·29
0·5345	1·5326	41·60	33·53
0·5423	1·5697	44·80	34·55
0·5576	1·5571	48·60	35·87
0·5260	1·5424	53·20	37·80
0·6255	1·5630	58·00	39·80
0·6308	1·5525	60·15	40·63
0·6186	1·4536	64·80	43·10
4·1810	6·7490	79·25	60·15*

Solubility in 87·73 *per cent Ethyl Alcohol.*

Weight of $HgBr_2$ in grms.	Weight of alcohol in grms.	Temp. °C.	Solubility in 100 gms. of alcohol.
0·3121	1·8123	32·90	17·22
0·3914	1·8258	42·13	21·44
0·4082	1·7822	45·20	22·91
0·4446	1·7538	49·07	25·35
0·5198	1·8596	55·85	28·61
0·5438	1·7082	61·60	31·84
0·5230	1·4094	68·97	37·11

Solubility in 99·88 *per cent Methyl Alcohol.*
(with Karam Chand Taxali).**

Weight of $HgBr_2$ in gms.	Weight of alcohol in gms.	Temp. °C.	Solubility in 100 gms. of alcohol.
1·0634	1·5578	22·10	67·62
1·5099	1·5965	27·40	68·81
1·1078	1·8770	30·80	70·25
1·1411	1·5846	36·10	73·31
1·1831	1·4058	49·80	84·43

* By Tschugaeff and Chlopin's method (*Z. anorg. Chem.*, 1914, **86**, 154).

† By direct precipitation as HgS.

** From Thesis in part fulfilment of M.Sc. Degree (1924) of the Punjab University.

The values are in agreement with the rule of Von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1128) that solubilities of salts in methyl alcohol are greater than in ethyl alcohol. The values obtained for the solubility in ethyl alcohol are consistently lower than those recorded by Timofeiew (*Dissertation*, 1894) whose paper is not available for comparison of the method and the strength of alcohol employed. The solubilities in methyl alcohol are higher than those obtained by the same author, but are in fair agreement with those given by Lloyd and others (*loc. cit.*).

On allowing a saturated solution of mercuric bromide in methyl alcohol to stand for a few hours, voluminous needle-like crystals developed in the tube, probably due to the formation of a methyl alcoholate. On analysis of the solid phase at the laboratory temperature, 1·4189 gms. gave Hg=50·86. $HgBr_2$, CH_3OH requires Hg=51·11 per cent.

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The Preparation of the Substituted Butyrolactams.

By Sarbbani Sahay Guha Sircar.

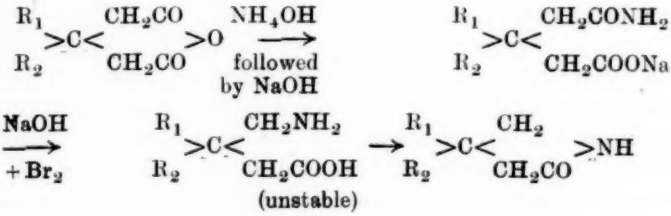
The following work was undertaken with a view to supplement the work already published in connection with the influence of groups and associated rings on the stability of certain heterocyclic ring systems (*J. Chem. Soc.*, 1227, **131**, 600, **1252**, 1257 ; *ibid.*, 1928, **133**, 898.) The systems previously studied under the above heading were, respectively, the substituted glutarimides, succinimides, paraconic acids and the butyro- and valero-lactones. Though the actual study of the relative velocity of the ring fission in the present series of compounds has not been found immediately possible owing to the unsatisfactory nature of the reactions so far studied with this end in view, the preparation and the properties of the compounds themselves are of sufficient interest to justify the present communication.

The preparation of a series of alkyl substituted γ- or δ-amino-acids or their lactams cannot be accomplished by the various methods already known for the preparation of such compounds (*cf.* Fischer, *Ber.*, 1904, **37**, 3063 ; 1906, **39**, 351 ; Gabriel, *Ber.*, 1891, **24**, 2452 ; 1908, **41**, 513, 1127, 2010; Mendius, *Ber.*, 1895, **28**, 1949; Engel, *Ber.*, 1875, **8**, 1597 ; Tafel, *Ber.*, 1886, **19**, 2414 ; 1894, **27**, 2313 ; Haller and Bauer, *Compt. rend.*, 1914, **158**, 1086 ; Blaise, C., 1899, [ii], 524 ; Wallach, *Annalen*, 1900, **312**, 171 ; Schotten, *Ber.*, 1883, **16**, 644) mainly on the ground of difficulty in obtaining the suitable intermediate compounds, specially in the case of the *gem*-dialkylated derivatives.

A simple way out of the difficulty would seem to be the reduction of the imides of the dibasic acids (glutaric and succinic) which might be expected to yield the lactams by the simple reduction of one of the carbonyl groups in these compounds, but a number of attempts at such reduction involving the use of zinc or tin and hydrochloric acid, iron and acetic acid, hydriodic acid (with or without phosphorous), or sodium and alcohol, failed to give the desired products. The difficulty seems to lie in the slow velocity of the reduction process as compared with the ease with which the imides hydrolyse into the corresponding acids and ammonia. Negative results were also obtained when the lactones corresponding to the lactams (Sircar, *loc. cit.*) were heated with urea or ammonia, or

when the silver salts of the imides were heated with ammonium iodide.

The various methods above described having failed to give the desired product, Hofmann's reaction, applied to the imides of the glutaric acids was ultimately resorted to. This method has been employed with success by Hoogewerf and van Dorp (*Rec. trav. Chim*, 1891, **10**, 4) in the case of phthalimide and succinimide, and has been improved upon by Lengfeld and Stieglitz (*Amer. Chem. J.*, 1906, **15**, 215, 518) who obtained a number of derivatives of β-aminopropionic acid, by its means. Noyes (*Ber.*, 1894, **27**, 917) introduced a slight variation in the procedure in the case of camphorimide by opening the imide ring with hot alkali before adding bromine. As, however, there is a large range of variation in the stabilities of the various substituted glutarimides (Sircar, *loc. cit.*) required for this purpose, the employment of hot alkali involves the risk of incomplete ring-fission in some cases, and the further hydrolysis of the first formed amic acid (into the glutaric acid and ammonia) in the others. To overcome this difficulty, it was found advisable to decompose the anhydrides of the various substituted glutaric acids (which are less stable than the imides in all cases) with ammonia, in order to form the amic acids. This reaction is fairly rapid and does not involve the risk of further change. The ammonium salts of the amic acids thus obtained were then converted into the corresponding sodium salts and the latter treated with hypobromite as in Hofmann's reaction. The details of the method will be found in the experimental portion. The following scheme give the series of reactions involved.



Experimental.

The substituted butyrolactams were prepared by a slight modification of Noyes' method applied to camphorimide. The suitable glutaric anhydride was treated with 2·2 equivalents of concentrated ammonia solution (sp. gr. 0·88), when a vigorous reaction ensued.

When this subsided, the mixture was heated on the steambath for 1½ hours to complete the reaction. The excess of ammonia was also removed in part by this treatment. After cooling, the ammonium salt of the amic acid was decomposed by a slight excess of equivalent amount of sodium hydroxide solution (10 per cent.) and the liberated ammonia removed under reduced pressure at 40-50°. This process was generally complete when the solution was concentrated to half its volume. The solution of sodium glutaramate thus produced was next added with stirring to a cold solution of potassium hypobromite made by dissolving one equivalent of bromine in 8 equivalents of 10 per cent. caustic potash solution (900 c.c. of 10 per cent. potash and 10 c. c. of bromine for ⅕ molecule of the anhydride). There is a small amount of effervescence at this stage due to a certain amount of free ammonia remaining in the solution. The mixture was then gradually heated in a water-bath to 70-75° and kept there for two hours.

When the reaction was over, the solution was somewhat concentrated by distilling off some water from a sand-bath. This procedure also decomposed any unchanged amic acid. The solution was then cooled and neutralised with concentrated hydrochloric acid after adding some sodium bisulphite to decompose the unchanged hypobromite. In the case of the diethyl and the *cyclo*hexane derivatives some of the lactam was at this stage thrown out and was extracted with ether. The solution itself was then strongly acidified with concentrated hydrochloric acid, and evaporated to dryness on the water-bath. The residue was introduced into an extractor and exhausted first with ether and then with alcohol or acetone, the former solvent removing some of the glutaric acid (formed from the amic acid). The acetone extract was evaporated to a pasty consistency to remove the excess of hydrochloric acid, dissolved in a small amount of water and carefully neutralised with 10 per cent. caustic soda solution in the cold. The mixture was then extracted with pure ether several times, the latter dried with potassium carbonate and distilled.

The lactams thus obtained can be distilled without decomposition under ordinary pressure, though the boiling points are fairly high, higher indeed than the corresponding butyro- and valerolactones. They are thick colourless liquids or low melting solids with a characteristic smell when liquid. They are moderately soluble in water and very soluble in all the usual organic solvents

including light petroleum. In all these solvents they tend to form supersaturated solutions and come out as fairly big flattened rhombic prisms. They are neutral in reaction and moderately stable towards dilute acids and alkalis. They are precipitated from aqueous solution by phosphotungstic acid (white precipitate), mercuric acetate (white), lead acetate (white), tannic acid (white), Meyer's reagent (yellow), or Dragendorff's reagent (deep brown). With 3:5-dinitrobenzoyl chloride in alkaline solution they give a deep violet colouration.

The butyrolactams form crystalline additive compounds with mercuric chloride in aqueous solution. These compounds, however, slowly decompose into their components on warming their solutions in water or organic solvents. Yellow oily gold chloride addition compounds are formed in ethereal solution, which could not be obtained in the crystalline condition. Yellow, oily or crystalline nitroso derivatives (nitrosamines) are obtained when the lactams are dissolved in dilute sulphuric acid solution and a solution of potassium nitrite is added in the cold. In the case of the higher members this derivative soon solidifies and can be crystallised from ether-petrol. The lower members are however liquids. All of them give the Liebermann reaction. The nitroso derivatives are gradually decomposed in warm aqueous solution, and much more rapidly in the presence of alkali. Unstable silver derivatives of the lactams are obtained by adding an alcoholic solution of silver nitrate to the sodio-derivatives formed by the addition of an equivalent of sodium ethoxide in alcohol to the lactams. On warming, these derivatives decompose, leaving a silver mirror.

The lactams also form crystalline benzoyl derivatives under Schotten-Baumann conditions. The lower members, however, form liquid derivatives.

cyclo*Hexane*spiro*butyrolactam* was obtained from *cyclo*hexane diacetic anhydride in 46 per cent. yield, m.p. 98°, b.p. 180-181°/13 mm. It crystallises in flattened tetrahedra from petrol (b.p. 40-60°). (Found: C, 70·45; H, 9·9; N, 9·0. $C_9H_{15}ON$ requires C, 70·6; H, 9·8; N, 9·1 per cent.). The *benzoyl* derivative crystallises from petrol in stout needles, m.p. 138°. (Found: C, 74·5; H, 7·3; $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4 per cent.). The *nitroso* derivative crystallises from petrol in needles, m.p. 82°. (Found: N, 15·2. $C_9H_{14}O_2N_2$ requires N, 15·4 per cent.). The mercuric chloride *addition product* melts at 158-160°.

cyclo*Pentane*spiro*butyrolactam* was obtained in 38 per cent. yield, m.p. 75°, b.p. 164°/16 mm. It crystallises from petrol in large flattened tetrahedra, and has a great tendency to form supersaturated solution in this solvent. (Found: C, 69·05; H, 9·2; N, 9·8. $C_8H_{13}ON$ requires C, 69·06; H, 9·35; N, 10·1 per cent.). The *benzoyl* derivative crystallises from petrol in needles, m.p. 70-71°. (Found: C, 73·8; H, 7·0. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0 per cent.). The *nitroso* derivative crystallises from petrol-ether in long needles, m.p. 51-52°. The mercuric chloride *addition compound* melts at 135°.

ββ-Dimethylbutyrolactam was obtained in 35 per cent. yield, m.p. 65-66°, b.p. 146-147°/12 mm. It crystallises from petrol in diamond-shaped crystals. (Found: C, 63·55; H, 9·7. $C_6H_{11}ON$ requires C, 63·7; H, 9·7 per cent.). The *benzoyl* derivative crystallises from petrol, m.p. 69°. The *nitroso* derivative melts at 45°. The lactam has also been described by Blaise (C., 1899, [*i*], 874).

ββ-Methylethylbutyrolactam was obtained in 30 per cent. yield, m.p. 74-75°, b.p. 150-152°/13 mm. (Found: C, 66·0; H, 10·2; $C_7H_{13}ON$ requires C, 66·14; H, 10·23 per cent.). The nitroso derivative is an oil which could not be solidified.

ββ-Diethylbutyrolactam was obtained in 40 per cent. yield, m.p. 76-77°, b.p. 163°/12 mm. (Found: C, 67·9; H, 10·5. $C_8H_{15}ON$ requires C, 68·1; H, 10·6 per cent.). The mercuric chloride *addition product* melts at 130°.

β-Ethylbutyrolactam was obtained in 25 per cent. yield, b.p. 117-118°/13 mm. (Found: C, 63·5; H, 9·5. $C_6H_{11}ON$ requires C, 63·7; H, 9·7 per cent.). The nitroso- and the benzoyl derivatives are liquids which failed to solidify.

β-Methylbutyrolactam was obtained in 15 per cent. yield, b.p. 116°/15 mm. (Found: C, 60·4; H, 8·8. C_5H_9ON requires C, 60·6; H, 9·1 per cent.).

Butyrolactam was obtained in 20 per cent. yield, b.p. 114°/14 mm. (Found: C, 56·4; H, 8·1. C_4H_7NO requires C, 56·5; H, 8·2 per cent.).

In attempting to apply the method of ring-fission employed in the other series of compounds (imides, paraconic acids and lactones, *loc. cit.*), it was unfortunately found that the lactam ring is very much more stable than the other rings so far studied. Thus equivalent alkali in N/200 or N/100 solution produced very little effect in three hours in the case of the first two members and even heating

in the presence of N/10 alkali for 5 hours at 55° produced fission to the extent of less than 10 per cent. A similar observation has been recorded in the case of oxindole by Baeyer (*Ber.*, 1883, **16**, 1704) who found that this lactam has to be heated with a solution of baryta to 150° in order to bring about complete fission. As the employment of such drastic conditions would necessarily take away the value of the quantitative data so obtained (by introducing disturbing factors), and especially as it would involve greatly increased difficulty of experimental manipulation, it was ultimately decided, after a number of unsuccessful attempts, to abandon the method rather than collect data of doubtful value by its means. The preparation of the lactams, however, is not without interest as very few members of this class of compounds are known and as their properties have not been studied in detail by any previous worker.

The author wishes to thank Professor J. F. Thorpe, C.B.E., D.Sc., F.R.S. for his kind interest in the work.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON.

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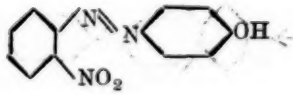
A New Synthesis of Derivatives of Benztriazole.

By Sachindra Nath Chakrabarty and Sikhibhushan Dutt.

Under the definition of benztriazoles are included those compounds which were formerly obtained by the action of nitrous acid on aromatic *o*-diamines, the first of which was prepared by Hoffmann (*Annalen*, 1860, **115**, 251) from *o*-diamino-nitrobenzene, and which was definitely proved by Griess (*Ber.*, 1882, **15**, 1878) to have the constitution (I). Subsequently Ullmann and Mauthner (*Ber.*, 1902, **35**, 4302 ; 1903, **36**, 4026), Curtius (*J. pr. Chem.*, 1907, (*ii*) **76**), Borsche (*Ber.*, 1921, **51B**, 660) and others have prepared derivatives of benztriazoles by different methods, but none seems to have found out a general way of synthesis of these derivatives. The present work is the outcome of an investigation undertaken in connection with the steric effect of chromophoric superposition on colour, which has been described in a separate communication. In connection with that investigation it was found that though *o*-nitro-azobenzene is very easily reduced to *o*-amino-azobenzene by alcoholic ammonium sulphide in normal manner, yet when *o*-nitro-benzene-azophenol (II) was similarly treated, instead of yielding the expected *o*-amino-benzene-azophenol, it gave an altogether different product which did not contain an amino group. On careful examination it was found that the product thus obtained was 2-(4-'hydroxyphenyl)- 1 : 2 : 3-benztriazole (III).

I.



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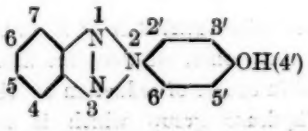
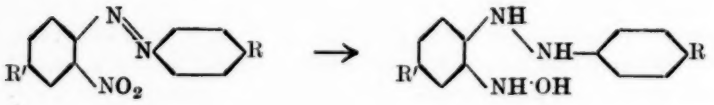


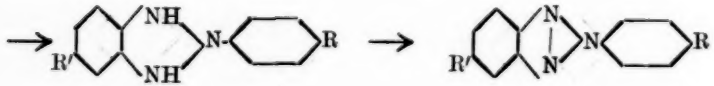
III.

It was then thought that the reactive hydroxy group in the *o*-nitrobenzene-azophenol had probably something to do in bringing about this peculiar reaction, and accordingly it was methylated and the reaction tried again. In this case also the same thing happened and the product was found to be 2-(4′-methoxy-phenyl)-1:2:3-benztriazole. So the reactivity of the hydroxy group in this connection was out of question. It was then thought that probably the weight of the substituent on the benzene nucleus containing the hydroxy group and not the reactivity of the latter was really responsible for this peculiar reaction, and accordingly an azo-dyestuff was prepared from diazotised aniline and *m*-nitraniline, which did not contain any substituent in the said benzene nucleus (IV, R′=NH_2, R=H). But when this substance was reduced with alcoholic ammonium sulphide, again a triazole derivative, namely, 5-amino-2-phenyl-1:2:3-benztriazole (VII, R=H, R′=NH_2) formed.

So the conclusion that can be derived from the results of these experiments is that though *o*-nitro-azobenzene undergoes reduction by ammonium sulphide, in a normal manner, to *o*-amino-azo-benzene, yet as soon as a substituent is introduced in any of the two benzene nuclei, the two latter are brought nearer to each other in space, with the result that the reduction takes a different course and a derivative of benztriazole is formed. The reaction probably undergoes the following course :



IV. V.

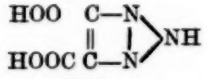


VI. VII.

In (V), the effect of substituent R or R′ is to bring the two benzene nuclei nearer to each other, so that the intermediate—NHOH group which is formed in course of reduction of the nitro group at once reacts with the hydrazo group which is also simultaneously formed by reduction of the azo group, with the result that a

dihydro benztriazole (VI) is formed, which spontaneously loses hydrogen and gets transformed into benztriazole (VII).

That the compounds described in this paper are real triazole derivatives was proved beyond doubt by oxidising 2-(4′-hydroxyphenyl)-1:2:3-benztriazole (III) with potassium permanganate in alkaline solution whereby triazole-dicarboxylic acid (VIII) was obtained, which was found to be identical with the acid obtained by Bladin (*Ber.*, 1893, **26**, 545) on oxidation of methyl-benztriazole.



VIII.

Experimental.

In the following series of experiments, *o*-nitraniline was first diazotised and coupled with various phenols and amino compounds in the usual manner. The azo-dyestuffs thus obtained were then treated with aqueous or alcoholic ammonium sulphide under suitable conditions whereby the azo compound was rapidly reduced and the corresponding benztriazole derivative obtained in very good, sometimes in almost quantitative yield.

2-(4′-*Hydroxy-phenyl*)-1:2:3-*benztriazole*.—Prepared from *o*-nitrobenzene-azophenol. Colourless silky needles from alcohol, m.p. 231°. (Found : N, 19·9. $C_{12}H_9ON_3$ requires N, 19·9 per cent.).

2-(4′-*Methoxy-phenyl*)-1:2:3-*benztriazole*.—Obtained from *o*-nitrobenzene-azophenol by first methylation with dimethyl sulphate in sodium hydroxide solution to *o*-nitrobenzene-azoanisol (yellow needles, m.p. 71°) and then reducing the latter with alcoholic ammonium sulphide. Colourless glistening plates from alcohol, melting at 138°. (Found : N, 18·5. $C_{13}H_{11}ON_3$ requires N, 18·7 per cent.).

2-(2′:4′-*Dihydroxy-phenyl*)-1:2:3-*benztriazole*.—Prepared from *o*-nitrobenzene-azoresorcinol (red powder, m.p. 185°). Pale brown silky needles from acetic acid melting at 191°. (Found : N, 18·9. $C_{12}H_9O_2N_3$ requires N, 18·5 per cent.).

2-(4′-*Hydroxy-naphthyl*)-1:2:3-*benztriazole*.—From *o*-nitrobenzene-azo-α-naphthol (red powder, m.p. 236°). It crystallises from alcohol in light yellow needles melting at 201°. (Found : N, 15·7. $C_{16}H_{11}ON_3$ requires N, 16·1 per cent.).

2-(2'-*Hydroxy-naphthyl*)-1:2:3-*benztriazole*.—From *o*-nitro-benzene-azo-β-naphthol (orange powder, m.p. 127°). Light brown needles from alcohol melting at 119°. Found: N, 16·5. $C_{16}H_{11}ON_3$ requires N, 16·1 per cent.).

2-(3'-*Carboxy*-4'-*hydroxyphenyl*)-1:2:3-*benztriazole*.—From *o*-nitro-benzene-azo-salicylic acid (reddish brown powder, m.p. 217°). Colourless needles from alcohol, melting at 300°. (Found : N, 16·6. $C_{13}H_9O_3N_3$ requires N, 16·5 per cent.).

2-(3'-*Carboxy*-4'-*hydroxy-naphthyl*)-1:2:3-*benztriazole*.—From *o*-nitrobenzene-azo-α-oxynaphthoic acid (purple powder, m.p. 168°). It crystallised from glacial acetic acid in light grey needles melting at 189°. (Found : N, 13·6. $C_{17}H_{11}O_3N_3$ requires N, 13·8 per cent.).

2-(4'-*Carboxy*-3'-*hydroxy-phenyl*)-1:2:3-*benztriazole*.—From *o*-nitrobenzene-azo-β-oxynaphthoic acid (red powder, m.p. 247°). It crystallised from alcohol in colourless silky needles melting at 109°. (Found : N, 13·6. $C_{17}H_{11}O_3N_3$ requires N, 13·8 per cent.).

2-(2': 3':4'-*Trihydroxy*-6'-*carboxy-phenyl*)-1:2: 3-*benztriazole*.—From *o*-nitrobenzene-azo-gallic acid (brown powder, m.p. 111°). The substance could not be crystallised. It was precipitated from alcohol as a yellow powder melting at 191°. (Found : N, 13·9. $C_{13}H_9O_5N_3$ requires N, 14·6 per cent.).

2-(4'-*Hydroxy*-3'-*aldehydo-phenyl*)-1:2:3-*benztriazole*.—From *o*-nitrobenzene-azo-salicylaldehyde (brown needles, m.p. 148°). It crystallised from alcohol in glistening yellowish white needles, m.p. 132°. (Found: N, 17·4. $C_{13}H_9O_2N_3$ requires N, 17·6 per cent.).

2-(4'-*Aminophenyl*)-1:2:3-*benztriazole*.—From *o*-nitrobenzene-azo-aniline (bright red needles, m.p. 195°). The substance crystallised from dilute alcohol in light yellow silky needles melting at 135°. (Found: N, 26·9. $C_{12}H_{10}N_4$ requires N, 26·6 per cent.).

The above substance on diazotising and boiling with water was converted into another substance melting at 231°, which was found to be identical with 2-(4'-hydroxy-phenyl)-1:2:3-benztriazole already described.

2-(4'-*Dimethylamino-phenyl*)-1:2:3-*benztriazole*.—From *o*-nitrobenzene-azo-dimethylaniline (red needles, m.p. 131°). Pale yellow needles from alcohol, melting at 187°. (Found : N, 23·1. $C_{14}H_{14}N_4$ requires N, 23·5 per cent.).

5-*Amino*-2-*phenyl*-1:2:3-*benztriazole*.—Prepared from benzene-azo-*m*-nitraniline (orange needles, m.p. 121°) by reduction with

ammonium sulphide. It crystallised from alcohol in yellowish white shining plates melting at 182°. (Found: N, 25·9. $C_{12}H_{10}N_4$ requires N, 26·6 per cent.).

5-Amino-2-(4'-sulpho-phenyl)-1:2:3-benztriazole.—Prepared from *p*-sulpho-benzene-azo-*m*-nitraniline (orange powder) by reduction with ammonium sulphide. It crystallised from glacial acetic acid in pale yellow silky needles. (Found: N, 18·9. $C_{12}H_{10}O_3N_4S$ requires N, 18·9 per cent.).

5-Amino-2-naphthyl-1:2:3-benztriazole.—From 1-naphthalene-4-azo-nitraniline (orange needles, m.p. 138°) by reduction with ammonium sulphide. Yellow needles from alcohol, melting at 169°. (Found: N, 21·1. $C_{16}H_{12}N_4$ requires N, 21·5 per cent.).

5-Amino-2-(2'-naphthyl)-1:2:3-benztriazole.—From naphthalene-2-azo-*m*-nitraniline (red powder, m.p. 169°) by reduction with ammonium sulphide. It could not be crystallised. It was obtained from alcohol in the form of a light brown powder, m.p. 114°. (Found: N, 21·4. $C_{16}H_{12}N_4$ requires N, 21·5 per cent.).

Oxidation of 2-(4'-Hydroxyhenyl)-1:2:3-benztriazole.

Five gm. of the above substance were dissolved in the requisite quantity of dilute sodium hydroxide and treated with a 5% solution of potassium permanganate in the cold until the latter was no longer decolorised. The precipitated manganese dioxide was filtered off and the filtrate evaporated to a small volume after neutralisation with dilute sulphuric acid. The liquid was then rendered strongly acid with dilute sulphuric acid when a crystalline precipitate was formed. The latter was filtered off and was identified to be triazole-dicarboxylic acid.

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Ionisation Potentials and Grating Energies of Atoms in the Solid State.

By Susil Chandra Biswas.

According to Bohr's theory, an electron revolving about its stable orbit is acted on towards the centric positive charge with a Coulombian force of attraction. The energy of such an electron orbit can be calculated as the sum of the potential energy and the kinetic energy of rotation of the electron. For a circular orbit it can be shown that the average kinetic energy of the electron in the atom is just one-half as great as the average potential energy, but the two act in opposite senses. This may mean that the sum total of energies of an orbit is potential in character, which gradually diminishes away from the centre to the limit of the field of force. The work done when an electron falls from infinity to the normal orbit is called the ionisation work, which will be a measure of the energy of the normal level of the atom. In the intermediate space also, there are a number of stationary orbits having, in suspension of the principles of electro-magnetic radiations, the peculiar "quantum condition" of the orbits which are radiation-less inspite of the revolution of the electrons in those orbits. In this sense, possibly, Langmuir (*Science*, 1921, **53**, 290) suggested that if in Bohr's theory a repulsive quantum force varying inversely as the cube of the distance is assumed, in addition to the Coulombian force of attraction, kinetic energy in Bohr's equation of orbital motion can be really substituted by a form of potential energy and the system reduces to a truly static one.

In crystalline solid bodies where arrangements of atoms are presumably static, such a law of force composed of an electrostatic force of attraction with a repulsive force following the inverse power law, *i.e.*, B/r^{n+1} (r representing the distance between the atoms) has been assumed by Born.* According to Madelung's (*Phys. Zeit.*, 1918, **19**, 524) calculation, the resultant potential energy under such

* Born—*Verh. d. D. Phys. Ges.*, (1918-1921); "Atom Theorie des Festen Zustandes," 1922.

a system of forces, in an electrical system of alternately positive and negative charges can be expressed as

$$W_{pot} = -\frac{A}{\delta}\left(1-\frac{1}{n}\right) \quad \ldots\ldots\ldots (1)$$

where A is Madelung constant, dependent on the lattice-type and δ the distance between the ions.

Relationship between Compressibility and Grating Energy.

If V represents the change in volume produced by the external pressure P, the total energy $W = W_{pot} + p.dV$.

The equilibrium condition requires that

$$\frac{dW_{pot}}{d\delta} + p.\frac{dV}{d\delta} = 0 \quad \text{whence } p = -\frac{1}{3\delta^2}.\frac{dW_{pot}}{d\delta}$$

By definition, compressibility of the crystal, β, is given by

$$\beta = -\frac{1}{V}.\left(\frac{dV}{dp}\right)_{T=o} = \frac{9\delta}{d^2W_{pot}/d\delta^2} = \frac{9\delta^4}{A(n-1)},$$

$$\text{or } \beta^{\frac{1}{4}} = \sqrt[4]{\frac{9}{A(n-1)}}.\delta \quad \ldots\ldots\ldots (2)$$

Combining (1) and (2)

$$\beta^{\frac{1}{4}}.\ W_{pot} = \frac{A(n-1)^{\frac{3}{4}}.\ 9^{\frac{1}{4}}}{n}$$

i.e., the product of the lattice energy and the fourth root of the compressibility of the elements will be a constant quantity depending on the lattice type and the unknown exponent of the repulsive force.

In the following table, the compressibilities of elements in the solid state will be compared to their potential energies in the gaseous state, *i.e.*, to their ionisation energies. From the constancies of the products, it appears that the compressibilities of elements in the solid state will be proportional to their values in the gaseous state and similarly the grating energies of the elements in the solid state will be proportional to their ionisation energies in the gaseous state. This latter view seems to be justified also by Eve's (*Nature*, 1921, **107**, 552) results in which the products of ionisation potentials and Bragg's diameters of combining atoms remain constant for the same group of atoms.

TABLE I.*

1			2	3	4	5
Mendeleef's groups.	Elements.	Structure.	I. P. (volts).	† Compressibility $\beta \times 10^{12}$	$\beta^{\frac{1}{2}} \times 10^{3}$.	I.P. $\times \beta^{\frac{1}{2}}$.
I A.	Li	B. C. C.	5·368	9·6	1·732	9·29
	Na	,,	5·11	15·1	1·98	10·12
	K	,,	4·32	31·5	2·37	10·23
	Rb	?	4·158	40·0	2·52	10·46
	Cs	?	3·877	61·0	2·76	10·82
I B.	Cu	F. C. C.	7·80	0·75	0·93	7·25
	Ag	,,	7·54	0·84	0·95	7·27
	Au	,,	9·125	0·47	0·81	7·39
II A.	Mg	H. C. P.	7·613	2·90	1·313	9·9
	Ca	F. C. C.	6·09	5·07	1·55	9·4
	Sr	,,	5·67	(10·6) (comp.)	—	10·2
	Ba	,,	5·19	(14·7) (comp.)	—	10·2
II B.	Zn	H. C. P.	9·353	1·5	1·11	10·36
	Cd	,,	8·955	1·9	1·174	10·51
	Hg(solid)	,,	10·39	1·13 (comp.)	—	10·7
III A.	Al	F. C. C.	5·96	1·33	1·07	6·40
III B.	Tl	F. C. C.	7·30	2·60	1·27	9·27
IV A.	C(diamond).	F. C. C.	11·20	1·16††	0·631	7·25
IV B.	Pb	,,	7·93	2·33	1·235	9·79
VII A.	Mn	,,	7·36	0·84	0·95	6·99
VIII.	Fe	,,	8·20**	0·4	0·79	6·48
	Ni	,,	9·90**	0·27	0·72	7·13

* Ionisation values are mostly taken from Franck-Jordan's "Anregung Von Quanten Sprungen," 1926.

Provisionally for Fe (Laporte, *Zeit. Physik*, **26, 18) and for Ni (Bechert and Sommer, *Ann. der Physik*, **77**, 359) are taken.

† Kaye and Laby, "Table of Constants", pp. 28, 29 (see compressibilities.)

†† Adams, *Washington Academy of Science*, 1921, **11**, 45.

Apparently in Table I (col. 5), two constants are found for two series of elements. Elements of Group IB have the same valency as the elements of Group IA and as regards their crystalline structure they represent elements of Group IIA. But it is interesting to find that the constants of Group IB differ from either of Group IA or Group IIA (Table I, col. 5). This clearly points out that the change in two series is mainly determined by the order of compression, a substance may undergo, or according as the exponential coefficient n is large or small (*vide* Haber's results, Table I, row 1). From the constancy of the products in the case of elements of Group II A & B the compressibility of Hg (solid) and those of Sr and Ba have been provisionally computed. The result for Al seems to be peculiar.

Metal Crystals.

Incidentally it has been assumed in the foregoing considerations that electrons inside a metal are arranged in space-lattices to form crystalline solids. Haber (*Sitzungsber.*, 1919, **506**, 990), on the assumption that in monovalent metal crystals structures are of haloid types in which only the negative ion has been replaced by an electron, determined the exponent of repulsive coefficient n from compressibility data and thence computed their grating energies (Table II, row 2). It was also shown that by vaporisation of metallic crystals, isolated atoms could be produced which were capable of subsequent ionisation.

$$[M] = (M) - D \quad \text{.....(sublimation)*}$$
$$(M) = (M^+) + \epsilon - J \quad \text{.....(ionisation)}$$
$$[M] = (M^+) + e - (D + J) \quad \text{.....(3)}$$

or the lattice energy $V_m = D + J$. Both these quantities are experimentally known and their calculated V_m is entered in Table II (row IV).

It may be seen (Table II, row 1) that Haber's n lies between 2·4 and 3·6 for alkali metals and between 8·0 and 9·0 for Cu, Ag, etc. This explains why different constants appear in Table I (col. 5) for the two series of metals. Exactly in the same way, on the assumption

* Here and in the following equations parenthesis ( ) refers to gaseous state and brackets [ ] to solid state.

of cubic structures for alkali metals, and on the assumption of a law of force $F = E.\ e\ /\delta^2(1-\frac{c}{\delta})$ where $c = 1{\cdot}75$, a distance at which the force changes from one of attraction to repulsion. Sir J. J. Thomson ("The Electron in Chemistry," p. 120) has calculated the compressibilities which are well within the range of experimental results. Calculated grating energies using J. J. Thomson's equation $V_m = -1{\cdot}825\ e^2/\delta$, computed by taking for δ the experimentally determined lattice distances * in A. U. (*e.g.*, Li, 3·50; Na, 4·30; K, 5·20) are given in Table II, row 3. Values for alkali metals as computed by J. J. Thomson, (*loc. cit.*, p. 121) determining δ from the cube root of molecular volumes seem to be too high.

TABLE II. **

		Li.	Na.	K.	Rb.	Cs.	Cu.	Ag.
I.	Computed n from compressibility (Haber).	2·44	2·9	3·18	3·64	3·62	8·0	9·0
II.	Computed grating energy V_m (volt) (Haber).	6·51	5·69	5·04	5·04	4·68	11·73	10·5
III.	Computed grating energy V_m (volt) (J. J. Thomson).	7·47	6·08	5·03	—	—	—	—
IV.	$V_m = (J + D)$ (volts) (experimental).	7·09	6·25	5·12	4·98	4·66	10·69	10·17
V.	$V_m = \phi_- + \varphi_{M_+}$ (volts) (experimental).	7·13	6·29	5·09	4·73	4·65	—	—

As metal crystals are supposed to be composed of electrons and positive residues as ions, the lattice energy can also be calculated from the work of dissociation of the crystal ions into gaseous ions. This can be shown as follows:—

$$[M] = [M^+] + \epsilon - \phi, \quad \text{.....(A)}$$ (evaporation of negative electrons).

$$[M^+] = (M^+) - \phi_{M^+} \quad \text{.....(B)}$$ (evaporation of positive ion).

* A. H. Compton, "X-Rays and Electrons," p. 116.

** Table II, rows (I, II and IV) are taken from *Handbuch der Physik*, Vol. 22, p. 437.

Adding together

$$[M]=(M^+)+e-(\phi_e+\phi_{M^+})$$

or $$V_m=\phi_e+\phi_{M^+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Both these quantities—energy of expulsion of electrons from solid metals (A) and that of evaporation of positive ions (B)—can variously be calculated.

Energy of expulsion of electrons from metals (Eqn. A) can be determined mainly from (*a*) the thermionic work function in Richardson's equation for electron emission where the thermionic current flowing per unit area per sec,

$$i=A.\,T^2.\,e^{-\phi_e/kT}$$

where A is a universal constant, k the gas constant and T the absolute temperature. It can be shown that ϕ_e in volts is related to Richardson's b by $\phi_e=8{\cdot}62\times10^{-5}\times b$, or from (*b*) photo-electric threshold frequency such that $e.\phi_e=h\nu_0$, ν_0 being the threshold frequency and h Planck's constant. It may be pointed that for alkali metals, the threshold frequency is not so definitely known, hence they are calculated from an approximate relation $\frac{3}{2}\nu_0=\nu_{max}$; ν_{max} stands for selective photo-electric effect according to Richardson's * theory of photo-electron emission.

ϕ_e expressed in volts as determined by either of the methods are given below :—

	Li.	Na.	K.	Rb.	Cs.
Volts.....	2·35	1·182 2·100	1·55	1·45	1·36

For the determination of the energy of evaporation of positive ions, the concept of Born and Fajans (*Ber. Deut. Phys. Ges.*, 1918, **20**, 712) regarding the heat of hydration of gaseous ions is of much practical use. Heat of hydration has been defined as the difference between the heat necessary for the dissociation of crystal ions into free gaseous ions and the 'heat of solution' of these ions in water. From a consideration of the electro-static energies of ions in vacuum and water, it can be shown that the electro-static energy of the gaseous ions will be ($K=81$) times greater than in solution or what means the

* Richardson, "Emission of Electricity from Hot Bodies," 1921, p. 41. Allen, "Photo-electricity," 1925, p. 168.

same thing that the heat of hydration of gaseous ions will be for all practical purposes identical to the heat of evaporation of positive ions.

Following a mode of calculation by Fajans, based on thermochemistry, the following method for the determination of the heat of hydration of gas ions has been worked out which is independent of the lattice energy concept.

According to Witmer (*Proc. Nat. Acad. Amer.*, 1926, **12**, 238) heat of dissociation for H_2 molecules (100,100 cals.)—

$$\tfrac{1}{2}(H_2) = (H) - 50{,}050 \text{ cal} \ldots\ldots \text{(dissociation of the molecule)}$$
$$(H) = (H^+) + e - 312{,}000 \text{ cal} \ldots\ldots \text{(ionisation of the atom)}$$

$$\tfrac{1}{2}(H_2) = (H^+) + e - 362{,}050 \text{ cals} \ldots\ldots\ldots\ldots\ldots\ldots (C).$$

Taking potassium as representative of any metal M, it can be shown that

$$[K] = (K) - 21{,}000 \text{ cal.}$$
$$(K) = (K^+) + e - 99{,}000 \text{ cal.}$$

The result of Eqn. (3); $[K] = (K^+) + e - 120{,}000$ cals.....(D)

$$[K] + aq = K^+_{aq} + OH^-_{aq} + \tfrac{1}{2}(H_2) + 48{,}100 \text{ cals. (chemical action.)}$$
$$H^+_{aq} + OH^-_{aq} = aq \quad \text{(heat of formation)}$$

$$[K] + H^+_{aq} = K^+_{aq} + \tfrac{1}{2}(H_2) + 61{,}700 \text{ cals.} \qquad (E)$$

Substituting Eqns. (C) and (D) in Eqn. (E),

$$(K^+) + H^+_{aq} = K^+_{aq} + (H^+) - 180{,}350 \text{ cals.}$$

or $$(H^+) - H^+_{aq} - (K^+) - K^+_{aq} = 180{,}350 \text{ cals.}$$

In other words, $W_{H^+} - W_{K^+} = 180{,}350$ cals., where W stands for heat of hydration of gas ions. This gives the heat of hydration as the difference in W for two anions. After checking these results with the heats of hydrations of individual gas ions determined experimentally from a knowledge of the absolute electrode potentials by Born (*Zeit. Physik*, 1920, **1**, 45) heats of hydrations of gaseous ions are expressed in equivalent volts by the expression,

$$\frac{W \times 300 \times 4{\cdot}7 \times 10^7}{eN} = V \text{ (volts)},$$

e being the electronic charge (E.S.U), N the number of molecules per gram molecule.

Energy of Evaporation of Positive Ions.

	Li.	Na.	K.	Rb.	Cs.
Volts.....	4·78	4·47	3·54	3·28	3·29.

Grating energy as calculated from the energy of sublimation of ions is entered in Table II, row V. The agreement between the results in rows IV and V clearly indicates that the process of ionisation of an individual gas atom is the same as that of the assemblage of ions in crystal lattices. Electron affinities in the two cases, however, must differ. In the cases of crystal ions, as more than one ion are packed together due to the mutual influence of neighbouring ions, the force of attraction is considerably reduced.

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Extinction Coefficients of Mixtures of Mercuric Chloride and Organic Acids in the Ultraviolet as Experimental Evidence in Favour of the Formation of Unstable Intermediate Compounds. Part III.

By J. C. Ghosh and T. L. Kasturi Rangacharya.

In previous papers by Ghosh and Mitra (*J. Indian Chem. Soc.*, 1927, **4**, 353; 1928, **5**, 191) it has been shown that the observed exaltations in the values of extinction coefficients when uranyl salt or ferric salt is mixed with organic acids, can be explained quantitatively on the hypothesis that an intermediate compound is produced by the association of one molecule of uranyl or ferric salt with one molecule of organic acid. The dissociation constant of these intermediate compounds and their extinction coefficients for several wave-lengths in the ultraviolet were calculated according to a method developed in those papers.

It is well known that almost all organic acids undergo photo-chemical decomposition in presence of mercuric chloride. The general mechanism of this photo-chemical decomposition is not yet definitely settled, and this investigation was undertaken with the object of finding out if the hypothesis of formation of intermediate compounds preliminary to photo-decomposition is supported by measurements of extinction coefficient of the photo-sensitive mixtures.

The experimental procedure and the methods of calculation are identical with those described before; and it may be stated at the outset that the experimental data recorded in the tables given in this paper can be quantitatively explained on the basis of—

(1) An equilibrium between mercuric chloride and an organic acid as reactants and the intermediate complex formed by the loose combination of one molecule each of the reactants.

(2) The assumption of a definite value of molecular extinction coefficients for each wave-length for the intermediate complex so formed.

Experimental.

The mercuric chloride and organic acids were carefully purified in the laboratory and the extinction coefficients were measured with the aid of the rotating sector photometer of Adam Hilger in conjunction with their quartz spectrograph.

Though the photographic density of the two spectra in juxtaposition can be compared fairly accurately, still the probability of error in the value of the extinction coefficients is certainly $\pm 7\%$.

The length of the tube containing the solution was 2 cm. in all cases.

The observations were always made with mixtures of salt and organic acid, where the acid was in excess, the ratio of acid/salt being generally not less than 5.

In the following tables, $K = \dfrac{\text{Conc. of intermediate compound}}{\left[\begin{matrix}\text{Conc. of } HgCl_2 \\ \text{unchanged}\end{matrix}\right]\left[\begin{matrix}\text{Conc. of unchanged} \\ \text{organic acid}\end{matrix}\right]}$

x = Conc. of intermediate compound;

E calc. = The calculated value of the extinction coefficient of the mixture, assuming a definite value of the molecular extinction coefficient $[E_M^{\lambda}]$ for each wave-length λ.

Table I.

M/1000 $HgCl_2$ and Formic Acid ($K = 10$).

	Log I_0/I_t for wave-length λ.				x calc. (conc. of intermediate complex).
λ.....2545		2507	2445	2400	
M/1000 $HgCl_2$	·05	·10	·25	·45	
M/2 acid	·10	·30	1·20	—	
Mixture	·35	·65	—	—	$·83 \times 10^{-3}$
E calc.	·35	·65	—	—	
M/5 acid	·05	·15	·60	1·35	
Mixture	·25	·45	1·05	—	$·67 \times 10^{-3}$
E calc.	·26	·45	1·05	—	
M/10 acid	—	·05	·30	·65	
Mixture	·15	·30	·70	1·40	$·50 \times 10^{-3}$
E calc.	·17	·30	·70	1·40	
M/20 acid	—	—	·15	·30	
Mixture	·10	·20	·50	·95	$·33 \times 10^{-3}$
E calc.	·13	·20	·50	·95	
M/40 acid	—	—	·05	·15	
Mixture	·10	·15	·35	·70	$·20 \times 10^{-3}$
E calc.	·10	·16	·36	·72	

In obtaining the values of E calc. K has been assumed to be 10 in all cases and the following values of E_M^λ given:

λ =	2545	2507	2445	2400
E_M^λ =	$\cdot145 \times 10^3$	$0\cdot20 \times 10^3$	$0\cdot275 \times 10^3$	$0\cdot525 \times 10^3$

With M/500-$HgCl_2$ and different concentrations of formic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K = 10$, and

λ =	2600	2545	2507	2445
E_M^λ =	$\cdot06 \times 10^3$	$\cdot15 \times 10^3$	$\cdot20 \times 10^3$	$\cdot27 \times 10^3$.

TABLE II.

M/1000 $HgCl_2$ and Acetic Acid ($K = 8$).

Log I_0/I, for wave-length λ.

λ	2507	2445	2400	2370	x calc.
M/1000 $HgCl_2$	·10	·25	·45	·65	
M/2 acid	·15	·55	1·25	—	
Mixture	·35	—	—	—	$\cdot80 \times 10^{-3}$
E calc.	·35	—	—	—	
M/10 acid	·05	·10	·25	·50	
Mixture	·20	·55	1·25	—	$\cdot44 \times 10^{-3}$
E calc.	·21	·55	1·25	—	
M/20 acid	—	·05	·15	·25	
Mixture	·15	·45	·95	—	$\cdot28 \times 10^{-3}$
E calc.	·14	·43	·95	—	
M/50 acid	—	—	·10	·15	
Mixture	·10	·30	·70	1·35	$\cdot14 \times 10^{-3}$
E calc.	·12	·31	·72	1·35	
M/100 acid	—	—	·05	·10	
Mixture	·10	·30	·55	1·00	$\cdot074 \times 10^{-3}$
E calc.	·11	·28	·58	1·00	

In obtaining the values of E calc. K has been taken as 8 for all cases and the following values of E_M^λ given:—

λ =	2507	2445	2400	2370
E_M^λ =	$\cdot113 \times 10^3$	$\cdot35 \times 10^3$	$\cdot845 \times 10^3$	$2\cdot32 \times 10^3$.

With M/500-$HgCl_2$ and different concentrations of acetic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K = 8$ and

λ =	2545	2507	2445	2400
E_M^λ =	$\cdot05 \times 10^3$	$\cdot1 \times 10^3$	$\cdot35 \times 10^3$	$\cdot85 \times 10^3$.

TABLE III.

M/1000 $HgCl_2$ and Propionic Acid ($K=5{\cdot}5$).

	Log I_o/I_t for wave-length λ.				x calc.
λ	2507	2445	2400	2370	
M/1000 $HgCl_2$	·10	·25	·45	·65	
M/10 acid	·10	·15	·20	·40	
Mixture	·30	·80	—	—	$·355 \times 10^{-3}$
E calc.	·30	·80	—	—	
M/25 acid	·05	·05	·10	·15	
Mixture	·20	·50	1·00	—	$·18 \times 10^{-3}$
E calc.	·20	·50	1·00	—	
M/50 acid	—	—	·05	·10	
Mixture	·15	·35	·75	1·20	$·099 \times 10^{-3}$
E calc.	·18	·36	·75	1·20	
M/100 acid	—	...	—	·05	
Mixture	·10	·30	·60	·95	$·052 \times 10^{-3}$
E calc.	·11	·31	·58	·93	
M/200 acid	—	—	—	—	
Mixture	·10	·30	·50	·75	$·027 \times 10^{-3}$
E calc.	·11	·28	·51	·77	

In obtaining the values of E calc. K has been taken to be 5·5 in all cases and the following values of E_M^{λ} given:—

λ =	2507	2445	2400	2370
E_M^{λ} =	$·19 \times 10^3$	$·685 \times 10^3$	$1·475 \times 10^3$	$2·595 \times 10^3$

With M/500-$HgCl_2$ and different concentrations of propionic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=5{\cdot}5$ and

λ =	2545	2507	2445	2400
E_M^{λ} =	$·05 \times 10^3$	$·19 \times 10^3$	$·69 \times 10^3$	$1·48 \times 10^3$

TABLE IV.

M/1000 $HgCl_2$ and Oxalic Acid ($K=125$).

	Log I_o/I_t for wave-length λ.			x calc.
λ	3064	2961	2878	
M/1000 $HgCl_2$	—	—	—	
M/10 acid	·10	·60	1·30	
Mixture	·35	1·35	—	$·926 \times 10^{-3}$
E calc.	·35	1·35	—	
M/20 acid	·05	·30	·65	
Mixture	·25	1·00	—	$·862 \times 10^{-3}$
E calc.	·28	1·00	—	
M/50 acid	—	·10	·25	
Mixture	·20	·65	—	$·714 \times 10^{-3}$
E calc.	·19	·68	—	
M/100 acid	—	·05	·15	
Mixture	·15	·50	1·15	$·555 \times 10^{-3}$
E calc.	·15	·50	1·15	
M/250 acid	—	—	·05	
Mixture	·10	·25	·65	$·333 \times 10^{-3}$
E calc	·09	·27	·65	

In obtaining the values of E calc. K has been assumed to be 125 in all cases and the following values of E_M^λ given:—

λ =	3064	2961	2878
E_M^λ =	$\cdot135\times10^3$	$\cdot405\times10^3$	$\cdot90\times10^3$

With M/500-$HgCl_2$ and different concentrations of oxalic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by putting $K=125$ and

λ =	3274	3064	2961
E_M^λ =	$\cdot02\times10^3$	$\cdot14\times10^3$	$\cdot4\times10^3$

TABLE V.

M/1000 $HgCl_2$ and Malonic Acid ($K=110$).

Log I_0/I_t for wave-length λ.

λ	2545	2507	2445	2400	x calc.
M/1000 $HgCl_2$	·05	·10	·25	·45	
M/10 acid	·05	·10	7·40	1·20	
Mixture	·30	·45	1·30	—	$\cdot92\times10^{-3}$
E calc	·30	·45	1·30	—	
M/20 acid	—	·05	·20	·60	
Mixture	·25	·40	1·05	—	$\cdot85\times10^{-3}$
E calc.	·24	·38	1·05	—	
M/40 acid	—	—	·10	·30	
Mixture	·20	·30	·85	—	$\cdot73\times10^{-3}$
E calc.	·21	·30	·87	—	
M/100 acid	—	—	·05	·15	
Mixture	·15	·25	·65	1·40	$\cdot52\times10^{-3}$
E calc.	·17	·24	·67	1·40	
M/200 acid	—	—	—	·10	
Mixture	·10	·20	·50	1·10	$\cdot36\times10^{-3}$
E calc.	·13	·20	·50	1·09	

In obtaining the values of E calc. K has been assumed to be 110 in all cases and the following values of E_M^λ given:—

λ =	2545	2507	2445	2400
E_M^λ =	$\cdot135\times10^3$	$\cdot186\times10^3$	$\cdot48\times10^3$	$\cdot99\times10^3$

With M/500-$HgCl_2$ and different concentrations of malonic acid extinction coefficients could be measured for higher wave-lengths and observed values reproduced by assuming $K=110$ and

λ =	·2600	2545	2507	2445
E_M^λ =	$\cdot05\times10^3$	$\cdot135\times10^3$	$\cdot19\times10^3$	$\cdot5\times10^3$

TABLE VI.

M/1000 $HgCl_2$ and Succinic Acid ($K=95$).

Log I_0/I, for wave-length λ.

λ.....	2507	2445	2400	2370	x calc.
M/1000 $HgCl_2$	·10	·25	·45	·65	
M/25 acid	—	·05	·15	·30	
Mixture	·15	·55	1·35	—	$·79 \times 10^{-3}$
E calc.	·15	·55	1·35	—	
M/100 acid	—	—	—	·05	
Mixture	·15	·40	·90	1·45	$·49 \times 10^{-3}$
E calc.	·13	·40	·91	1·45	
M/150 acid	—	—	—	—	
Mixture	·10	·35	·80	1·25	$·39 \times 10^{-3}$
E calc.	·12	·37	·82	1·25	
M/500 acid	—	—	—	—	
Mixture	·10	·30	·60	·90	$·16 \times 10^{-3}$
E calc.	·11	·30	·60	·90	

In obtaining the values of E calc. K has been assumed to be 95 in all cases and the following values of E_M^{λ} given:—

λ =	2507	2445	2400	2370
E_M^{λ} =	$·082 \times 10^3$	$·283 \times 10^3$	$·699 \times 10^3$	$1·1 \times 10^3$

With M/500-$HgCl_2$ and different concentrations of succinic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=95$ and

λ =	2545	2507	2445	2400
E_M^{λ} =	$·03 \times 10^3$	$·08 \times 10^3$	$·28 \times 10^3$	$·70 \times 10^3$

TABLE VII.

M/1000 $HgCl_2$ and Glycollic Acid ($K=22$).

Log I_0/I, for wave-length λ.

λ	2600	2545	2507	2445	x calc.
M/1000 $HgCl_2$	—	·05	·10	·25	
M/5 acid	·30	·35	·35	·50	
Mixture	1·15	1·45	—	—	$·815 \times 10^{-3}$
E calc.	1·15	1·45	—	—	
M/10 acid	·15	·20	·20	·25	
Mixture	·85	1·15	1·25	—	$·688 \times 10^{-3}$
E calc.	·87	1·14	1·25	—	
M/20 acid	·05	·10	·10	·15	
Mixture	·60	·80	·90	1·45	$·524 \times 10^{-3}$
E calc.	·60	·82	·92	1·45	
M/50 acid	—	·05	·05	·10	
Mixture	·30	·50	·55	·95	$·306 \times 10^{-3}$
E calc.	·32	·50	·57	·96	
M/100 acid	—	—	—	·05	
Mixture	·20	·30	·35	·65	$·18 \times 10^{-3}$
E calc.	·19	·28	·35	·66	

In obtaining the values of E calc. K has been assumed to be 22 in all cases and the following values of E_M^λ given :—

λ =	2600	2545	2507	2445
E_M^λ =	$\cdot522\times10^{-3}$	$\cdot669\times10^{-3}$	$\cdot741\times10^{-3}$	$1\cdot13\times10^{-3}$

With M/500-$HgCl_2$ and different concentrations of glycollic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=22$ and

λ =	2722	2690	2600	2545
E_M^λ =	$\cdot37\times10^{-3}$	$\cdot40\times10^{-3}$	$\cdot52\times10^{-3}$	$\cdot70\times10^{-3}$.

TABLE VIII.

M/1000 $HgCl_2$ and Lactic Acid ($K=12\cdot5$).

Log I_0/I_t for wave-length λ.

λ.....	2545	2507	2445	2400	x calc.
M/1000 $HgCl_2$	·05	·10	·25	·45	
M/10 acid	·05	·10	·35	·70	
Mixture	·35	·60	—	—	$\cdot555\times10^{-3}$
E calc.	·35	·60	—	—	
M/25 acid	—	·05	·15	·30	
Mixture	·20	·40	1·00	—	$\cdot333\times10^{-3}$
E calc.	·20	·39	1·00	—	
M/50 acid	—	—	·10	·15	
Mixture	·15	·25	·70	1·40	$\cdot200\times10^{-3}$
E calc.	·14	·24	·71	1·40	
M/100 acid	—	—	·05	·10	
Mixture	·10	·20	·50	1·00	$\cdot111\times10^{-3}$
E calc.	·10	·18	·50	·99	
M/200 acid	—	—	—	·05	
Mixture	·10	·15	·35	·75	$\cdot059\times10^{-3}$
E calc.	·08	·14	·36	·74	

In obtaining the values of E calc. K has been assumed to be 12·5 in all cases and the following values of E_M^λ given:—

λ =	2545	2507	2445	2400
E_M^λ =	25×10^{-3}	$\cdot41\times10^{-3}$	$1\cdot03\times10^{-3}$	$2\cdot23\times10^{-3}$

With M/500-$HgCl_2$ and different concentrations of lactic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=12{\cdot}5$ and

λ =	2600	2545	2507	2445
E_M^λ =	$\cdot11\times10^3$	$\cdot25\times10^3$	$\cdot41\times20^3$	$1{\cdot}03\times10^3$

TABLE IX.

M/1000 $HgCl_2$ and Tartaric Acid ($K=31$).

Log I_o/I_t for wave-length λ.

λ	2600	2545	2507	2445	x calc.
M/1000 $HgCl_2$	—	·05	·10	·25	
M/10 acid	·05	·10	·20	1·05	
Mixture	·25	·55	1·10	—	$\cdot758\times10^{-3}$
E calc.	·25	·55	1·10	—	
M/50 acid	—	—	·05	·20	
Mixture	·10	·25	·55	—	$\cdot383\times10^{-3}$
E calc.	·10	·25	·55	—	
M/100 acid	—	—	—	·10	
Mixture	·05	·15	·35	1·40	$\cdot137\times10^{-3}$
E calc.	·06	·18	·35	1·40	
M/200 acid	—	—	—	·05	
Mixture	·05	·10	·25	·90	$\cdot134\times10^{-3}$
E calc.	·04	·12	·24	·90	
M/500 acid	—	—	—	—	
Mixture	—	·10	·15	·50	$\cdot058\times10^{-3}$
E calc.	·02	·08	·16	·51	

In obtaining the values of E calc. K has been assumed to be 31 in all cases and the following values of E_M^λ given :—

λ =	2600	2545	2507	2445
E_M^λ =	$\cdot132\times10^3$	$\cdot289\times10^3$	$\cdot579\times10^3$	$2{\cdot}344\times10^3$

With M/500-$HgCl_2$ and different concentrations of tartaric acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=31$ and

λ =	2690	2600	2543	2507
E_M^λ =	$\cdot035\times10^3$	$\cdot132\times10^3$	$\cdot289\times10^3$	$\cdot579\times10^3$

TABLE X.

M/1000 $HgCl_2$ and Mandelic Acid ($K=70$).

Log I_0/I, for wave-length λ.

λ.....2961		2878	2824	2770	x calc.
M/1000 $HgCl_2$	—	—	—	—	
M/5 acid	·05	·35	·40	·80	
Mixture	·30	·75	1·15	—	$·933 \times 10^{-3}$
E calc.	·30	·75	1·15	—	
M/20 acid	—	·10	·10	·20	
Mixture	·20	·45	·70	—	$·777 \times 10^{-3}$
E calc.	·21	·43	·72	—	
M/50 acid	—	—	·05	·10	
Mixture	·15	·25	·55	·75	$·583 \times 10^{-3}$
E calc.	·16	·25	·52	·75	
M/100 acid	—	—	—	·05	
Mixture	·10	·10	·35	·50	$·412 \times 10^{-11}$
E calc.	·11	·18	·33	·51	
M/200 acid	—	—	—	—	
Mixture	·05	·10	·20	·30	$·259 \times 10^{-3}$
E calc.	·06	·11	·21	·29	

In obtaining the values of E calc. K has been assumed to be 70 in all cases and the following values of E_M^{λ} given:—

λ =	2961	2878	2824	2770
E_M^{λ} =	$·134 \times 10^3$	$·215 \times 10^3$	$·402 \times 10^3$	$·557 \times 10^3$

With M/500-$HgCl_2$ and different concentrations of mandelic acid extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=70$ and

λ =	3064	2961	2878	2824
E_M^{λ} =	$·13 \times 10^3$	$·134 \times 10^3$	$·215 \times 10^3$	$·402 \times 10^3$

Inferences.

The following regularities, similar to those obtained in work with uranyl nitrate and ferric chloride (*loc. cit.*) in the value of the dissociation constant K of the intermediate complex, have been obtained in this case also.

(*i*) In a homologous series the value of K diminishes for each successive addition of a CH_2 group:—

Oxalic/Malonic = 125/110 = 1·14 ; Malonic/Succinic = 110/95 = 1·86;
Formic/Acetic = 10/8 = 1·25; Acetic/Propionic = 8/5·5 = 1·45.

(*ii*) The value of K increases very much in replacing a hydrogen atom of the CH_3 group by a COOH group.

Oxalic/Formic = 125/10 = 12·5 ; Malonic/Acetic = 110/8 = 13·7;
Succinic/Propinic = 95/5·5 = 17·3.

(*iii*) In the case of a monobasic acid replacement of a hydrogen atom of the CH_3 group by an OH group increases the value of K.
Glycollic/Acetic = 22/8 = 2·75 ; Lactic/Proopionic = 12·5/5·5 = 2·27.

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Interaction of Chlorosulphonic Acid with Substituted Amides of Cyanacetic Acid.

By K. G. Naik and M. B. Amin.

The aim with which this piece of work was undertaken was to study the reactivity of the two hydrogen atoms of a reactive methylene group situated between a cyanogen group and a carbonyl group, as in the case of substituted amides of cyanacetic acid. Attempts were already made to study the reactivity in the case of substituted amides of malonic acid using sulphur monochloride and sulphur dichloride as reagents by Naik (*J. Chem. Soc.*, 1921, **119**, 379, 1231), by Naik and Avasare (*ibid*, 1922, **121**, 2592, 2595), by Naik and Patel (*J. Indian Chem. Soc.*, 1924, **1**, 27), by Naik and Jadhav (*J. Indian Chem. Soc.*, 1926, **3**, 259). Attention is here confined to the study of the interaction of some of the substituted amides of cyanacetic acid using chlorosulphonic acid as the reagent.

It is well-known that chlorosulphonic acid reacts with many organic compounds giving rise to sulphonic derivatives. In fact the reagent has been often employed in the preparation of such compounds (Thorpe's "Dictionary of Applied Chemistry," Vol V. p. 301).

Reference to previous work* clearly shows that chlorosulphonic acid was principally used either in sulphonating aromatic compounds or in the preparation of sulphonyl chlorides. It was expected that here, too, the chlorosulphonic acid would attack the hydrogen atoms of the reactive methylene group and give rise to sulphonic acid derivatives. The experimental evidence recorded in this paper bears this out.

* Hemilian (*Ber.*, 1873, **6**, 196); Claessen (*Ber.*, 1881, **14**, 307); Hodgkinsen and Mathews (*Ber.*, 1883, **16**, 1103); Limpricht (*Ber.*, 1885, **18**, 2172); Traube (*Ber.*, 1890, **23**, 1634); Reinhard (*J. pr. Chem.*, **125**, 332); Stewart (*J. Chem. Soc.*, 1923, **123**, 2384, 2388); Jacob, Pollak, Fulneggand Reiz (*Monatsh.*, 1926, **46**, 383, 397); Krasjinovie (*Ber.*, 1926, **59**, 2117, 2719).

An attempt is also made here to shew that the reactivity of these hydrogen atoms depends, in some measure, on the sumtotal negativity of the groups adjoining the reactive methylene group.

Interaction of chlorosulphonic acid with the following susbtances was studied:—

Cyanacetanilide ;	cyanacet-benzylamide ;
cyanacet-*p*-toluidide ;	cyanacet-α-naphthylamide ;
cyanacet-*o*-toluidide ;	cyanacet-β-naphthylamide ;
cyanacet-*m*-toluidide ;	cyanacet-xylidide (1:4:5).

The first sulphonic acid of the series enumerated above was prepared by reacting cyanacetanilide with chlorosulphonic acid, using dry salicyl chloroform prepared according to Anschütz's method (*Annalen*, 1893, **273**, 94 ; *Ber.*, 1892, **25**, 3501, 3512), as the medium of interaction. Salicyl chloroform, so prepared, has no action on chlorosulphonic acid at its boiling point.

During the course of the interaction, neither sulphonyl chlorides nor sulphones of the aromatic substituted amides of cyanacetic acid could be isolated. In all the cases sulphonic acid derivatives were obtained and the reagent attacked the methylene group.

Cyanacetanilide, readily interacted with chlorosulphonic acid, thus:

$$CN{\cdot}CH_2{\cdot}CONHPh + 2ClSO_3H = CN{\cdot}C(SO_3H)_2{\cdot}CONHPh + 2HCl. \qquad (I)$$

That the constitution assigned to (I) is correct, and that all the sulphoacids, derived from the various amides enumerated above, can be generally so represented follows from the considerations given below.

(1) That the hydrogen atoms eliminated during the course of the interaction are not those which were originally attached to the nucleus, because on hydrolysis with alcoholic caustic potash, *p*-toluidine was obtained as one of the products of hydrolysis from the corresponding sulpho-acid which was derived from cyanacet-*p*-toluidide.

(2) The results of the above hydrolysis also point to the fact that the hydrogen atoms replaced by the sulphonic groups are not those which were originally attached to the nitrogen atoms, as in that case, *p*-toluidine could not have been found as one of the products of hydrolysis.

(3) Further, on attempting to brominate the sulpho-acid (I) the two HSO_3 groups were found to have been replaced by two bromine atoms, as was apparent from subsequent reduction of the di-bromo derivative, both the bromine atoms being easily reduced by Kurt Meyer's method. This clearly proves that the bromine atoms were attached to the methylene carbon atom, and hence, the original sulphonic groups which were replaced by these bromine atoms, also had been attached to the methylene carbon atom.

The three cyanacet-toluidides, cyanacet-benzylamide and cyanacet xylidide and cyanacet-naphthylamides react in a similar manner with chlorosulphonic acid giving analogus sulphonic acid derivatives. But in the cases of the naphthylamides a longer time was required before the reaction was complete.

In relation to the question of the reactivity of the hydrogen atoms of the methylene group with regard to chlorosulphonic acid it may be said that the experimental observations afford a clear evidence that the avidity of the interaction of chlorosulphonic acid with the substituted amides depends on the total negativity of the groups attached to the two remaining valencies of the methylene carbon atom. In the case of cyanacetamide in which one of the valencies of the methylene carbon atom carries the neutral group, $(-CONH_2)$, no reaction takes place. But when the neutral character of this group is disturbed by the entrance in it of a phenyl, a tolyl, a benzyl, a naphthyl or a xylyl group, the reactivity starts.

Although no definite measurements have been made, it is evident from the experiments recorded here, that the rapidity with which the reaction proceeds in these cases depends on the electronegative character of the groupings attached to the methylene carbon atom. Thus in a series like this—

(1) $CN\text{-}CH_2\text{-}CONH_2$, (2) $CN\text{-}CH_2\text{-}CONHC_6H_5$,
(3) $CN\text{-}CH_2\text{-}CONHC_7H_7$, (4) $CN\text{-}CH_2\text{-}CONHC_8H_9$,
(5) $CN\text{-}CH_2\text{-}COOEt$,

the reactivity which is absent in (1), starts with (2), and goes on increasing through the series.

The mechanism of the interaction studied here is interesting. In such cases where both the hydrogens of the methylene group are replaced by sulphonic groups when the reaction starts, the substance may be supposed to assume an enolic form (Norris and Thorpe, *J. Chem. Soc.*, 1921, **119**, 1203).

Experimental.

Disulphocyanacetanilide.—Cyanacetanilide (3 g.) was mixed in a flask with 25 c.c. of salicyl chloroform and an excess of chlorosulphonic acid (5 g.) was added. A vigorous reaction started with evolution of heat and hydrogen chloride. The flask was kept overnight and refluxed the next day in order to complete the reaction. When the evolution of hydrogen chloride ceased and the superfluous chloroform was taken out, 100 c.c. of distilled water were added to the syrupy product and the mixture was boiled. The syrupy mass went into solution and was finally filtered to free it from any unaltered cyanacetanilide. The filtrate deposited shining leaflets, which were washed repeatedly with alcohol in which they were almost insoluble. Finally the product was recrystallised from water. During the course of this investigation it was observed that in all the cases molecular proportions of the reactants did not give a good yield of the final product. An excess of chlorosulphonic acid gave quite satisfactory results, the chance of the amide remaining unreacted being thus completely eliminated.

The pure substance was found to be almost insoluble in alcohol, chloroform, carbon disulphide, carbon tetrachloride, acetone, benzene, toluene, ether and light petroleum. It was extremely soluble in hot water. It had no m.p. but charred above 270°. (Found: S, 16·06; H_2O, 18·3; N, 7·65; Eqv. wt., 197. $C_9H_8O_7N_2S_2,4H_2O$ requires S, 16·32; H_2O, 16·36; N, 7·16 per cent. Equiv. wt., 196.)

In the following preparations 5 g. of chlorosulphonic acid and 3 gms. of the substituted amides were employed. The products were purified as in the previous case. In solubility and other physical properties they resembled disulphocyanacetanilide.

Disulphocyanacet-p-*toluidide*, crystallised from water in colourless shining leaflets. It had no definite m.p. but darkened and charred at about 270°. Water of crystallisation $=2H_2O$, of which the compound loses half a molecule of water (2·91 per cent.) at 120°. (Found: S, 17·1. $C_{10}H_{10}O_7N_2S_2,2H_2O$ requires S, 17·29; loss of water, 2·43 per cent.).

Disulphocyanacet-o-*toluidide* had no definite m.p. but charred at 255-265°. (Found: S, 17·0. $C_{10}H_{10}O_7N_2S_2,2H_2O$ requires S, 17·29 per cent.).

Disulphocyanacet-m-*toluidide* crystallised in colourless shining scales. It has no definite m.p. but chars between 260° and 270°. (Found: S, 16·96. $C_{10}H_{10}O_7N_2S_2,2H_2O$ requires S, 17·29 per cent.).

Disulphocyanacet-α-naphthylamide crystallised from hot water. It has no definite m.p. but chars between 270° and 280°. (Found: S, 16·46. $C_{13}H_{10}O_7N_2S_2$, H_2O requires S, 16·49 per cent.).

Disulphocyanacet-β-naphthylamide was purified by crystallisation from hot water. It formed shining yellowish stout needles, which had no definite m.p. but charred between 270° and 280°. (Found: S, 15·80. $C_{13}H_{10}O_7N_2S_2,H_2O$ requires S, 16·49 per cent.).

Disulphocyanacetbenzylamide formed colourless plates, which charred between 265° and 275°. (Found: S, 17·3. $C_{10}H_{10}O_7N_2S_2,2H_2O$ requires S, 17·29 per cent.).

Disulphocyanacetxylidide (1 : 4 : 5) crystallised in the form of colourless light shining scales. It has no definite m.p. but chars between 270° and 280°. (Found: S, 17·4. $C_{11}H_{12}O_7N_2S_2,2H_2O$ requires S, 17·48 per cent.).

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Condition of Iodic, Hydrofluoric and Chromic Acids and their Salts in Aqueous Solution.

By N. R. Dhar.

In this communication I shall show that iodic and hydrofluoric acids and their salts exist mainly as $H_2I_2O_6$ and $M_2I_2O_6$, and H_2F_2 and M_2F_2. The ions given out from iodic acid and its salts are in the bivalent condition and are to be represented as I_2O_6'' and those given out from fluorides exist as F_2''.

I have also discussed the condition of chromic acid in aqueous solution and determined the second dissociation constant of this acid from solubility experiments.

Iodic Acid and Iodates.

In 1874 J. Thomsen came to the conclusion from various arguments that unlike chloric and bromic acids, iodic acid is dibasic and should be represented by $H_2I_2O_6$. Rosenheim and Liebknecht (*Liebig's Annalen*, 1899, **308**, 40) and Groschuff (*Ziet. anorg. Chem.*, 1906, **47**, 33) determined the molecular conductivity and the freezing point lowering and the elevation of the boiling points of solutions of iodic acid and the following values of *i* (Van't Hoff's coefficient) were obtained :—

v	1	2	3	4	5·3	16
i (electric conductivity)	1·43	1·53	—	1·63	—	1·81
i (cryoscopic)	0·95	1·21	—	1·41	—	1·67
i (ebullioscopic)	—		1·16	—	1·21	—

Hence it appears that iodic acid has a tendency to exist in the polymerised state. This conclusion is also supported from the following equivalent conductivity results of chloric and iodic acids.

V ...	2	4	8	16	32	64	128	256	512	1024
Chloric acid...	353	364	373	381	387	391	399	402	402	402
Iodic acid ...	192	230	268	301	328	350	364	372	377	380

The conclusion regarding the condition of iodic acid in aqueous solution from the above physico-chemical results has been corroborated from coagulation experiments performed with positively charged ferric hydroxide solution and iodic acid and iodates. Giolitti (*Gazzetta*, 1905, **35**, II, 181 ; 1906, **36**, II, 157, 433) observed that considerable amounts of HCl, HBr, HI, HNO_3 $HClO_4$ and $HBrO_3$ must be added to ferric hydroxide solution in order to effect precipitation. The hydroxide came down as a brick red powder which was peptised by water when the acid was washed out. He found further that traces of sulphurous, selenious, iodic, periodic and phosphoric acids and salts effected precipitation. Under these conditions he observed that the precipitate was gelatinous and did not redissolve on washing.

Weiser and Middleton (*J. Phys. Chem.*, 1920, **24**, 30) working with a solution of ferric hydroxide containing 1·54 grs. Fe_2O_3 per litre obtained the following precipitation values of potassium salts :—

		Amount required.	Precipitation value in milliequivalents.
Ferrocyanide	...	1·05 c. c. N/100	0·275
Ferricyanide	...	1·10 ,, ,,	0·287
Sulphate	...	1·70 ,, ,,	0·437
Oxalate	...	1·85 ,, ,,	0·475
Chromate	...	2·55 ,, ,,	0·650
Iodate	...	3·55 ,, ,,	0·900
Bromate	...	2·40 " N/2	31·3
Thiocyanate	...	3·65 ,, ,,	46·9
Chloride	...	8·00 ,, ,,	103·1
Chlorate	...	9·00 ,, ,,	111·6
Nitrate	...	10·25 ,, ,,	131·2

With acids the following results were obtained by Weiser and Middleton:

Acid.	Electrolyte.	Precipitation values in milliequivalents.
Dichromic ...	0·75 c. c. N/100	0·200
Tartaric ...	1·85 ,, ,,	0·475
Sulphuric ...	1·90 ,, ,,	0·485
Citric ...	1·90 ,, ,,	0·500
Oxalic ...	2·05 ,, ,,	0·525
Iodic ...	2·35 ,, ,,	0·600
Phosphoric ...	3·40 ,, ,,	0·875
Hydrochloric ...	16·0 ,, N/2	200·0
Nitric ...	17 0 ,, ,,	212·5
Formic ...	5·5 ,, 2N	275·0

Very recently Weitz and Stamm (*Ber.*, 1928, **61**, 1144) obtained the following comparative results with ferric hydroxide solution and different sodium salts:—

Sodium salt.	Chloride	Nitrate	Acetate	Fluoride	Iodate	Sulphate
Precipitation value.	1050	275	100	30	6·7	1

The foregoing results show that the precipitation values of iodate ion from iodic acid or iodates of sodium and potassium are of the same order as those of bivalent ions. Hence from experiments on coagulation we can conclude that iodic acid and iodates exist in aqueous solution at least partly as $H_2I_2O_6$ and $M_2I_2O_6$ and give out bivalent I_2O_6'' ions.

Hydrofluoric Acid and Fluorides.

It is well konwn that the determination of the vapour density of hydrofluoric acid at the ordinary temperature shows that there is molecular association in the gaseous condition. Moreover, the boiling point of liquid hydrofluoric acid is much higher than those of liquid HCl, HBr and HI and this proves that hydrofluoric acid in the liquid condition is associated.

Jäger (*Zeit. anorg. Chem.*, 1901, **27**, 28) from the reaction between hydroflouric acid and mercuric oxide, and Abegg *ibid*, 1903, **35**, 137) from the reaction between hydrofluoric and boric acids concluded that hydrofluoric acid in acqueous solution consists mainly of H_2F_2.

Pellini and Pegoraro (*Zeit. Elektrochem.*, 1907, **13**, 621) conclude that the conductivity of the acid with successive additions of alkalis shows a maximum when alkali equivalent to half a mole of hydrofluoric acid has been added and there is an abrupt change in the slope of the conductivity curve when an equivalent of alkali has been added. This behaviour is characteristic of typical dibasic acids and hence it might be assumed that hydrofluoric acid is dibasic.

Kremann and Decolle (*Monatsh.*, 1907, **28**, 917) have concluded from electric conductivity measurements of sodium fluoride that the acid is dibasic, although the measurements of Kohlrausch and co-workers (*Das Leitvermogen*, 1916, 146) with fluorides of sodium and potassium do not agree with the results of Kremann and Decolle. Deussen (*Zeit. anorg. Chem.*, 1905, **44**, 300, 408) has assumed that hydrofluoric acid consists of a mixture of HF and H_2F_2 molecules. Hans Pick (W. Nernst's " Festschrift " 1912, p. 360) has assumed that HF molecules unite with F' ions forming a complex HF_2'.

The view that hydrofluoric acid and fluorides are associated in aqueous solution has recently been supported from coagulation experiments on different colloids with potassium fluoride. Ghosh and Dhar (*Kolloid Zeit.*, 1928, **44**, 149; *J. Indian Chem. Soc.*, 1928, **5**, 303) showed that the precipitation values of potassium fluoride on sols of ferric hydroxide, ceric hydroxide, zirconium hydroxide, thorium hydroxide, chromium hydroxide and aluminium hydroxide are of the same order as those of potassium sulphate or oxalate. Similar result has very recently been obtained by Weitz and Stamm (*loc. cit.*) with ferric hydroxide sol and sodium fluoride.

Hence it appears that hydrofluoric acid and fluorides exist in aqueous solution at least partly as H_2F_2 and M_2F_2.

Chromic Acid and Chromates.

In a previous paper (*Zeit. anorg. Chem.*, 1922, **121**, 99) I have advanced the view that chromic acid exists in solution mainly as H_2CrO_4. The first dissociation constant of this acid is exceedingly high and the second dissociation constant is very small. I have now determined the second dissociation constant of chromic acid from the increase in the solubility of carbonic acid gas in solutions of potassium chromate (compare Datta and Dhar, *J. Chem. Soc.*, 1915, **107**, 824). The following results were obtained at 30°.

Original concentration of K_2CrO_4.	Original concentration of CrO_4'' ions.	Concentration of $HCrO_4'$ ions.	Final concentration of CrO_4'' ions.	Concentration of H° ions.	Second dissociation constant of chromic acid.
1·000 N	0·5837	0·3124	0·2713	$\frac{3\times10^{-7}\times\cdot056}{0\cdot3124}$	$4\cdot66\times10^{-8}$
0·500 N	0·3175	0·2016	0·1159	$\frac{3\times10^{-7}\times\cdot056}{0\cdot2016}$	$4\cdot79\times10^{-8}$

Hence, it will be seen that the second dissociation constant $\left(\frac{H^\circ\times CrO_4''}{HCrO_4'}\right)$ of chromic acid is exceedingly small and that this is why all normal chromates are alkaline towards indicators.

Sherrill (*J. Amer. Chem. Soc.*, 1907, **29**, 1641) determined the second dissociation constant of chromic acid and by conductivity and partition coefficient methods and obtained the value $7\cdot4\times10^{-7}$ at 25°.

Koppel and Blumenthal (*Zeit. anory. Chem.*, 1907, **53**, 228) determined the boiling points of aqueous solutions containing increasing amounts of CrO_3. In the following table, I have calculated the values of *i* from the measurements of Koppel and Blumenthal.

CrO_3 in 100 g. of water.	Observed b. p.	'*i*' calc. as H_2CrO_4	'*i*' calc. as $H_2Cr_2O_7$
12·12	102°	2·95	5·90
31·72	104°	2·25	4·50
57·40	107°	2·17	4·34
82·36	110·5°	2·17	4·34
120·05	116°	2·38	4·76
159·92	120°	2·23	4·46
247·7	127°	1·95	3·9

The foregoing results show that when CrO_3 is dissolved in water, the resulting solution exists mainly as H_2CrO_4 and H° and $HCrO_4'$, and CrO_4'' ions and not as $H_2Cr_2O_7$ and H° and Cr_2O_7'' ions. Similarly the measurements of the freezing points of solutions of chromic acid by Sherrill (*loc. cit.*), Kremann (*Wien. Akad. Ber.*, 1911, **120**, *iib*, 339), Büchner and Prins (*Zeit. physikal. Chem.*, 1913, **81**, 113) and Cornec (*Ann. Chim. Phys.*, 1913, (8) **29**, 491; **30**,

63) are more in support of the view that chromic acid is mainly H_2CrO_4 and not $H_2Cr_2O_7$. It is quite possible that in concentrated solutions and in presence of acids, we may get some $H_2Cr_2O_7$ molecules and Cr_2O_7'' ions, but in dilute solutions and in presence of alkali H_2CrO_4 and CrO_4'' ions are stable. Recently we have shown that sols of silicic, vanadic, molybdic and tungstic acids become less polymerised in presence of small quantitities of alkalis, and in presence of acids the polymerisation is increased.

Moreover, from Walden's measurements (*Zeit. physikal. Chem.*, 1888, **2**, 49) it will be seen that the difference between the equivalent conductivities of a solution of potassium dichromate at a dilution of 1024 and 32=10·2, whilst the value is 20·8 for potassium chromate. This shows that potassium dichromate in aqueous solution exists mainly as $KHCrO_4$.

Not much light regarding the constitution of chromic acid and chromates is thrown by the experiments on coagulation of ferric hydroxide sol by chromic acid and its salts. With aluminium hydroxide sol however, some interesting results have been obtained by Weiser and Middleton (*J. Phys. Chem.*, 1920, **24**, 630) and they are as follows.

Precipitation Values of Potassium Salts.

	Amount required.	Precipitation values in milliequivalents.
Ferricyanide	1·50 c.c. N/100	0·400
Citrate	1·70 ,,	0·438
Sulphate	2·10 ,,	0·538
Oxalate	2·75 ,,	0·700
Chromate	5·15 ,,	1·300
Dithionate	6.4 ,,	1·625
Dichromate	7·0 ,,	1·775
Chloride	11·0 c.c. N/2	143·7

According to the view advanced in a previous paper a solution of potassium dichromate is likely to be partly decomposed in water according to the following equation:—

$$K_2Cr_2O_7 + H_2O \rightleftarrows 2KHCrO_4.$$

Hence the precipitation value of dichromate should be greater than that of chromate, because from a dichromate solution the amount of CrO_4'' is less than that available from a solution of chromate of equivalent concentration. Recently Weitz and Stamm (*loc. cit.*) have obtained the following results on the coagulation of ferric hydroxide sol :—

Salt.	NaCl	Na_2SO_4	$K_2S_2O_3$	NaH_2PO_4	Na_2HPO_4
Precipitation value.	920	1	1	0·7	0·5

It will be evident that the precipitation value of sodium dihydrogen phosphate is appreciably greater than that of disodium hydrogen phosphate, because more divalent and trivalent negative ions are available from the latter salt than the former.

It is well known that a solution of disodium hydrogen phosphate is alkaline towards phenolphthalein and a solution of sodium dihydrogen phosphate is practically neutral. The precipitation values of both these phosphates are appreciably smaller than those of the divalent negative ions. It appears therefore that the few trivalent phosphate ions which are available from the (above) phosphate solutions exert their influence on the coagulation of ferric hydroxide and thus the precipitation values of both disodium hydrogen phosphate and sodium dihydrogen phosphate are smaller than those of the bivalent anions. Moreover, from the foregoing considerations it will be clear that though the precipitation value of potassium chromate on aluminium hydroxide sol is smaller than that of potassium dichromate, the two precipitation values should not differ highly, because the few CrO_4'' which will be given out from $HCrO_4'$ will exert their influence on the coagulation of the sol.

Summary.

1. Measurements of electric conductivity, lowering of freezing point and elevation of boiling point of solutions of iodic acid show that it is partly polymerised. Experiments on coagulation with ferric hydroxide sol and iodates and iodic acid show that iodate ions exist in the bivalent conditions as I_2O_6''. Similarly the view that

hydrofluoric acid and fluorides are associated in aqueous solution is supported from coagulation experiments on different sols. The precipitation values of potassium fluoride and potassium iodate on positively charged sols is of the same order as those of potassium sulphate and oxalate.

2. The second dissociation constant of chromic acid is very small and is of the order 5×10^{-8}. Electric conductivity and coagulation experiments are in favour of the view that potassium dichromate in solution exists partly as $KHCrO_4$.

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On the Method of Moving Boundaries as Applied to the Measurement of the Absolute Velocity, and the Transport Number of Ions and of the Rate of Migration of Colloidal Particles.

By Jnanendra Nath Mukherjee.

The theory of the moving boundary as put forth by Kohlrausch (Wied, *Ann.*, 1897, **62**, 209; see also Weber, *Sitz. Kon. Preuss. Akad. Wiss.*, Berlin, 1897, 935) and the experiments of Masson (*Phil. Trans.*, 1899, **192**, 331), of Steele (*Z. physikal. Chem.*,1902, **40**, 689) and of Dennison (*Z. physikal. Chem.*, 1903, **44**, 575; *Trans. Farad. Soc.*, 1909, **5**, 165) lead one to believe that a *stable boundary* can be realised when the slower moving ion follows the faster moving ion such that both move with equal speed. It has been repeatedly observed however that even in simple cases of two uni-univalent electrolytes having a common ion this condition is not sufficient (Steele, *loc. cit.*; Abegg and Gauss, *Z. physikal. Chem.*, 1902, **40**, 737; MacInnes and co-workers, *J. Amer. Chem. Soc.*, 1923, **45**, 2246; 1924, **46**, 1398; 1919, **41**, 994, 1009; 1927, **49**, 1710; see also H. S. Taylor, "Treatise on Physical Chemistry," Vol. I, pp. 547-49) and disturbing causes have been observed to operate which are not contemplated in this theory. A satisfactory explanation has so far not been obtained for these difficulties. It appears that apart from the case considered by Millar (*Z. physikal. Chem.*, 1909, **69**, 436) where the conditions on the two sides of the boundary are such that ions in one layer when they cross the boundary interact with ions in the other layer to form undissociated molecules and apart from the volume changes resulting from the concentration changes referred to by G. N. Lewis (*J. Amer. Chem., Soc.*, 1910, **32**, 862) the theoretical considerations underlying the theory on which these measurements are based have escaped a close scrutiny. MacInnes and co-workers remark (*loc. cit.*, **49** 1715), "As explained in previous papers in this series, the ions of the leading solution and the indicator move at the same rate when the solutions are adjusted to the condition $C/T = C'/T'$ ... (1) *

* C, C′ are the concentrations and T, T′ the transport numbers respectively of the cations of the two electrolytes (with a common anion) which meet at the boundary.

which must be in general obtained by a series of experiments..... According to Kohlrausch and others the condition represented by Equation (1) should establish itself automatically, no limits of initial concentration being stated. However, we have found in general that this can only be relied on for deviation of 3 to 5 per cent. from the correct concentration. There are apparently additional influences, including diffusion that limit the range of adjustment." In their papers references to other difficulties will be found. Steele (*loc. cit.*) also refers to numerous difficulties specially regarding the production, maintenance and movement of a sharp boundary.

The method of moving boundaries is of greater importance for the measurement of cataphoretic velocity of colloidal particles as in contrast to the case of electrolytic ions this method constitutes at present the most suitable direct method available.

Kohlrausch's Theory of Moving Boundaries.

Let us consider the simplest case of a boundary between two uni-univalent electrolytes AR and BR with a common anion R and further suppose that they are strong electrolytes in dilute solutions. Kohlrausch deduces the following relation regarding the rate of change of concentration of ions of one type with time *in the interior of either of the electrolytes* as the unidirectional current of constant strength i passes through the solution :—

$$\frac{\delta a}{\delta t} = -i.\, f\,(a)\frac{\delta a}{\delta N} \qquad \ldots \quad (2)$$

where δa is the change in concentration in the infinitesimal interval of time δt; $\delta a/\delta N$ is the rate of change in concentration of the ion species under consideration obtaining during the interval δt along the direction N of the current and $f(a) = \delta n/\delta a$ where δn is the change in the transport number of the ion (a cation) when the concentration of the ion (or the electrolyte) changes by δa. In deducing this relation Kohlrausch assumes that the electrolytic neutrality in the interior of the solution is satisfied under all conditions, and he states: "*Freie Ionen Können daher unter keinern Umständen im Inneren von Lösungen entwickelt werden*, sondern nur an metallisch leitenden Electroden" (p. 214). This condition must be satisfied if Ohm's Law is to remain valid. It is not necessary to overlook the existence of

free ions of both signs freely moving in the solution. All that is necessary is that in a surface at right angles to the direction of the current, the condition of electrical neutrality should be satisfied. Kohlrausch next considers the possibility of the existence of excess ions of one sign at the boundary itself and concludes (p. 216): "Auch die Ionenmengen der Helmholtz'schen Doppelschichten, welche den Sprung des Potentials an der Berührungsstelle verschiedenartigen Electrolyte bewirken, sind, selbst wenn man Contact in Molecularabständen annimmt, so klein, dass sie zur Leitung nicht merklich beitragen.

Die "freien Ionen" werden hiernach die Stromvorgänge nicht in wahrnehmbarem Maasse beeinflussen."

It will be seen that Kohlrausch (from his calculations) consider that "free ions" (excess of ions of one sign) need not be taken into consideration. Kohlrausch next considers the case of a dilute solution of several electrolytes and deduces the following relation,

$$\frac{\alpha}{a}+\frac{\beta}{b}+\ldots\ldots\ldots+\frac{\rho}{r}+\ldots\ldots\ldots=\text{a constant} \qquad \ldots \quad (3)$$

which is independent of time; where α, β,.....are the concentrations of the cations, ρ,..... are the concentrations of the anions, a, b,..... the mobilities (assumed to be constant) of the cations and r.....are the mobilities of the anions and remarks (p. 222), "Diese Summe möge *beharrliche Function* heissen." In fact this is the fundamental equation on which Kohlrausch bases his further treatment of the subject. Applying the above relation to the case of a mixture of several electrolytes with an ion of one sign in common, he obtains when the electrolyte is contained in a cylinderical tube with parallel layers of varying concentrations at right angles to the axis of the tube, the following relation:

$$\frac{\alpha}{n}+\frac{\beta}{n_B}+\ldots\ldots\ldots\ldots=\text{a constant, independent of time...} \quad (4)$$

Equation (4) signifies that the sum of the ratios of the concentration to the transport number for all the ions when the mobilities are constant and independent of concentration remains unaffected by the passage of the current. *In these discussions Kohlrausch so far assumes a continuous change in concentration from point to point.* Taking the case of a boundary between two single electrolytes AR

and BR at any section normal to the direction of the current and *in the interior of each electrolyte* relationships

$$\frac{\alpha}{n_A} + \frac{\rho}{n_R} = \text{constant} \quad \ldots \quad (5) \qquad \frac{\beta}{n_B} + \frac{\rho}{n'_R} = \text{constant} \quad \ldots \quad (6)$$

must be independent of time. But it does not follow necessarily from Kohlrausch's treatment that this relationship will remain valid for the discontinuous transition at the boundary of the two electrolytes AR and BR. Kohlrausch recognises this and remarks (p. 235): "Es mögen noch einige Bemerkungen uber den Fall folgen, dass verschiedene Lösungen mit scharfen Grenzen aneinander stossen, wobei der Unstetigkeit wegen die Folgerungen aus den Differentialgleichungen nicht ohne weiteres gelten."

Kohlrausch in effect considers the case of a sharp transition between two electrolytes as being a limiting case of continuous transition. He treats particularly the discontinuous transition between two different concentrations of a single electrolyte and of a dilute mixture of several electrolytes with a common ion. He points out that in these cases the relationship in Equation (3) remains valid. In connection with the case of a boundary that is, a discontinuous transition from concentration α_1 to concentration α_2 of a single electrolyte AR Kohlrausch remarks (p. 235): "Es treten von der einen Seite gerade soviele Ionen heran, wie auf der anderen Seite abgeführt werden." It is evident that the validity of Ohm's Law is assumed for the boundary and is considered to be a sufficient condition for the applicability of Equation (3) at the boundary for such sharp transitions. Regarding the case of a sharp transition between two electrolytes AR and BR, it appears that Kohlrausch does not definitely claim the validity of relation (3) but first considers that a sharp boundary exists and shows that the relation $\alpha/n_A = \beta/n_B$ must be satisfied. He remarks further (p. 238): "Man sieht, dass diese Betrachtung zu derselben Bedingung fuhrt, wie die vorige : die oft genannte beharrliche Function muss zu beiden Seiten der Grenze denselben Werth haben." Kohlrausch concludes (p. 239): "Diese und ähnliche Falle lassen sich, *wenn man die Voraussetzung macht, dass die Lösungen sich mit scharfen Grenzen verdrängen*, leicht construiren und die Resultate erscheinen als specielle Falle von Folgerungen aus der Differential

Gleichungen. *Ob aber die wandernden Grenzen scharf bleiben*, ist eine Frage, die durch besondere Betrachtungen uber die Unstetigkeitsstellen entschieden werden muss. Nach einer mir ebenfalls von Heinrich Weber mitgetheilten Betrachtung ergeben sich auch andere Möglichkeiten."

Weber (*loc. cit.*) basing his considerations on these assumptions subjects these cases of non-uniform (sharp) transitions to a more rigorous mathematical treatment and obtains the general result that for the case of a *mixed solution* of two electrolytes AR and BR a non-uniformity at any cross section of the expression $\frac{\alpha}{n_A} + \frac{\beta}{n_B}$ must remain at the same place during the passage of the current. Weber shows further that for a general solution based on the differential equations of Kohlrausch even in this simple case (p. 939) the movement of regions of discontinuities requires special treatment and concludes (p. 942): "Auf Grund der bisher gemachten Voraussetzungen lässt sich mathematisch nicht entscheiden, welche von aller diesen Lösungen dem wirklichen verlauf am meisten entspricht. Physikalisch dürfte aber doch wohl der stetigen Lösung der Vorzug zu geben sein, zumal wenn man, wie es ja der Wirklichkeit entspricht, die Unstetigkeit nur als idealen Grensfall eines sehr schnellen stetigen überganges betrachtet." *On the above assumption of a* discontinuous transition being a limiting case of continuous transition for the boundary between the two electrolytes AR and BR it is shown by Weber that when the slower moving ion follows the faster moving ion the concentrations on both sides of the boundary automatically adjust themselves to satisfy Equation (1) and the boundary remains stable.

Let us consider the transfer of ions across these boundaries with a view to examine closely how far we are justified in treating discontinuous transitions as a limiting case of continuous transitions. Kohlrausch (see particularly p. 235, also Weber *loc. cit.* p. 940) refers to the transference of ions across the boundary normal to the axis of the cylinder on both sides of which there is *a sharp transition* of concentrations either *of the single electrolyte AR or of the mixed solutions of electrolytes AR and BR.* In the latter case Kohlrausch mentions that the *total number of the ions A and B taken together* that enters the layer is equal to that which leaves it. The case of the sharp boundary between two concentrations of the *same electro-*

lyte is simpler and the above statement holds good. This is an essential condition so that Ohm's Law might be applicable. And this condition remains true whether the transition is continuous or discontinuous so long as Equation (3) holds good.

We shall see in the next section that in contrast to the above instances this condition is not satisfied in the case of a boundary between AR and BR even when Equation (1) is satisfied, and it constitutes the main reason why such a discontinuous transition cannot be taken as the limiting case (*i.e.*, only differing in degree) of a continuous transition.

The Validity of Ohms Law near the Boundary between two Electrolytes AR and BR when the slower Moving Ion follows the faster Moving Ion and Both move at the same Speed.

We shall now consider in detail the transference of the anion R across the boundary between AR and BR of concentrations C and C' respectively between which the relationship of equation (1) obtains. The condition that both ions would move at the same speed as also the condition that the differential equations of Kohlrausch are valid at the boundary require that the potential gradients in the layer on the two sides of the boundary and immediately contiguous to it must be inversely proportional to the mobility of the cation. As the slower moving ion is following the faster moving ion, for obvious reasons, there cannot be any mixing of the two cations. We should thus have a sharp boundary. The anion R is also simultaneously moving through the tube with the negative current and whereas B cannot overtake and cross the boundary to the layer of electrolyte AR or *vice versa*, the ions R are crossing the boundary at each instant under consideration. Now the actual speed of the ions R in the two layers are in the ratio of the potential gradients, that is, they are inversely proportional to the mobility of the cations in the layers (*cf.* Equation 1). Evidently the number of ions R coming from the layer of electrolyte AR (containing the faster moving cation A) into the layer of electrolyte BR immediately contiguous to the boundary will not be equal to the number of ions R coming from BR to AR. unless the concentrations of ions R in the two layers are inversely proportional to the potential gradient in each layer.

Referring to Figure I we find that the number of ions R crossing the

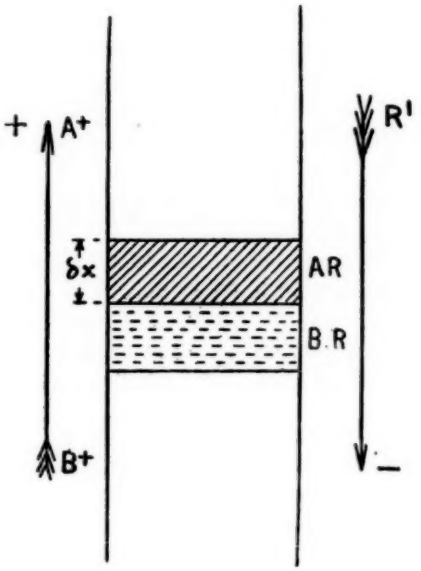

Figure 1.

boundary and entering into the immediately contiguous layer of electrolyte BR will be given by

$$i.\ (n_R)^{AR}.dt$$

where i denotes the *current density* and $(n_R)^{AR}$ is the transport number of the ion R in the electrolyte AR. We are assuming that during the interval dt the concentrations of AR and BR remain the same and the condition of electrical neutrality holds good on both sides of the boundary. These ions coming from the layer AR will spread into a thickness dx in the layer BR given by the relation:

$$dx = V'_R dt \qquad \ldots\ldots (7)$$

where V'_R is the actual speed of the ions R in the layer BR and is given by $P_{BR}.V_R$, where P_{BR} is the potential gradient in the layer BR and V_R is the mobility of the ion R per unit potential gradient,

The number of ions leaving the layer of BR of thickness dx contiguous to the boundary in the interval dt is given by $i.(n_R)^{BR}.dt$. Since $(n_R)^{BR}$ is greater than $(n_R)^{AR}$ the layer of volume dx contiguous to the boundary and containing the slower moving cation will be poorer (negative sign) in R by

$$-i.\left\{(n_R)^{BR}-(n_R)^{AR}\right\}dt \qquad (8)$$

Substituting the value of dt in (7) we have:

$$-i.\left\{(n_R)^{BR}-(n_R)^{AR}\right\}\frac{dx}{P_{BR}.V_R} \qquad (9)$$

Evidently there will always be a *defect* in the number of anions in the layer of BR contiguous to the boundary unless the term within the bracket is equal to zero. The condition for an equality in the transport numbers is either—

(*a*) That the two cations must have the same mobility, or (*b*) that the mobility of the anion is so great compared to that of the cations that the transport number of the anion is the same in both cases.

Taking the value of i to be 5 milli-amperes (per sq. cm.) which is about one-tenth of the current density used by MacInnes and the boundary to be between hydrochloric acid and lithium chloride we find that the number given by Equation (9) is several times greater than the total number of ions in the volume dx, or in other words the volume dx would contain only positive charges and the electrical density will be enormous. On account of the free motion of the ions in the liquid it is evident that the consequent enormous value of the non-uniform potential gradient will oppose the separation of electricity, and in effect a drag will act on the ions preventing a separation of electricity. There is therefore no escape from the conclusion that the fundamental differential equations of Kohlrausch, based as they are on the assumption of electrical neutrality and the validity of Ohm's Law, are not applicable to the layer on the side of the boundary containing the electrolyte BR. The sharpness or diffused character of the boundary will be greatly affected by the relationships discussed above.

The condition in the layer of the electrolyte AR is, however, in contrast to that in the electrolyte BR and the ions A travel in a 'uniform ionic environment.' The ions R always pass by the ions A along the direction of the negative current at a rate governed by the conditions in the single electrolyte AR. The actual speed of the ions A (or R) in two layers of different concentrations of AR whether the transition is continuous or discontinuous will be directly proportional to the potential gradients which in any two layers of the same electrolyte must be inversely proportional to the concentrations of the electrolyte obtaining in them. It follows that the actual speed will be inversely proportional to the concentrations. The total number f the ions A (or R) leaving any layer will be proportional to the roduct of the concentration in the layer and the actual speed. Since the actual speeds of the ions are inversely proportional to the concentrations, the product of the actual speed and the concentration is constant for all layers and the number of ions entering or leaving any layer lying wholly within the electrolyte AR will therefore be constant and independent of the position of the layer. Thus at the boundary between AR and BR the ion A always moves through the electrolyte AR and as the ions R which pass them come from the single electrolyte AR, *the ionic environment* of the ions A remains unchanged with the passage of the current. The position is however different regarding the ions B and R. We thus see that the effect of the electrical separation discussed above would least influence the movement of A but would considerably influence the movement of B and R in a manner not contemplated by Kohlrausch.

These conclusions are in complete agreement with the observations recorded in the literature. We find that the boundary method is recognised not to give correctly the actual speed of the ions. As usually used the rate of motion of two boundaries are simultaneously observed and it is always the motion of the faster moving ion that is measured. Experimental arrangements are always such that the faster moving ions move into a single electrolyte consisting of these ions and having a constant concentration* although Steele (*loc. cit.*, pp. 699-700) lays down the following conditions in order that correct values of the transport numbers comparable to those obtained by the usual methods may be obtained :—

(1) The mobility of the indicator ion must be smaller than that of the ion whose transport number is being measured.

* The liquid junction potential is thus non-existent inside the electrolyte.

(2) The indicator ion should not produce a precipitate with the solution under investigation.

(3) During the electrolysis no such ions must come into being which moves faster than the ion under measurement.

(4) The specifically lighter solution must be on the top of the heavier one.

(5) The resistance of the indicators should not be much greater than that of the solution which it follows.

(6) The potential gradients must lie within certain limits depending on the nature of the solutions which form the boundary.

It will be seen that conditions (5) is exactly what is implied in Equation (8). Steele considered that the observed difficulties originated from the heat developed on the passage of the current. While this is, no doubt, an important factor as has been emphasised by MacInnes it is clearly not a sufficient explanation in the numerous instances where the boundary remains sharp and perfectly horizontal. Some of these difficulties are summed up in condition (6) which along with condition (5) is not contemplated in the formulae of Kohlrausch and Weber. This has been pointed out by Steele who has investigated the conditions for a sharp boundary somewhat in detail. He attributes the difficulties in part to diffusion. From our experiments on cataphoresis it appears that convection currents on account of unequal changes in density destory a sharp boundary. MacInnes considered this heating effect as also diffusion but finds that they are not sufficient to explain the want of adjustment postulated by Kohlrausch.

The effect of the unequal movement of the anions just considered would amount to a drag on the slower moving cation and the anion. It has been pointed out already that Kohlrausch considers that the quantities of free ions associated with liquid junction potentials are negligible so far as their effect on the conduction of electricity and on Ohm's Law is concerned. It would appear that this asumption is not justifiable for all liquid junctions specially during the conduction of electricity as we have seen above that the electric current tends to produce an excess of one of the ions. And thus increase the potential drop at the junction. From Equation (9) it seems reasonable to assume that the boundary will be sharp and will move at a steady rate when the potential gradients on the BR sides of the boundary have so adjusted themselves that the same number of chlorine ions leave and enter the layer of electrolyte BR contiguous

to the boundary and necessarily the condition for production and maintenance of such a boundary would depend on the potential gradients in the two layers and on the transport numbers of the ion R in the two electrolytes. It should be stated that we are not considering in detail the effects of diffusion and of the densities of the two layers and their variations on the passage of the current. As to the exact nature of the conditions at the boundary, several possibilities arise. It is intended to consider these in a separate investigation.

To sum up, it appears from the above considerations that in the homogeneous solution AR with two specifically lighter indicator solutions BR and AR′ on its top as usually arranged in such experiments the ions A and R will be moving at the two boundaries

$$\leftarrow AR \mid \quad BR \text{ and } AR' \mid \quad AR \rightarrow$$

through a uniform ionic environment and if the potential gradient, or the current density and the concentration in the solution AR of constant strength be known their transport numbers can be determined: because though the drag at the boundary may have a disturbing effect its magnitude will be very small inside the electrolyte AR. But the adjustments at the bounday will not be governed by the equations of Kohlrausch and Equation (1) is not alone sufficient to characterise a satisfactory boundary. The current density and the transport numbers of the anion in the two layers are important factors. It also follows from Equation (9) that even in those cases where it is possible to determine the transport numbers by the boundary method, the movement of the boundary does not necessarily give the correct mobilities of both ions unless the transport number of the common ion has the same value in both electrolytes. The consideration of Kohlrausch and of Weber really do not postulate the difference between the two electrolytes AR and BR which underlies the conception of specifying the electrolyte with the slower moving ion as the 'indicator' solution. *One should from their theory expect the movement of the boundary to give correctly the mobilities of both ions.* It is well known to workers on this subjects that the boundary method is not at all suitable for this purpose. On the other hand it follows from the foregoing considerations in agreement with experience, that the usual method is suitable for the measurement of transport number of ions but not for the determination of absolute velocities.

The Boundary Method and Cataphoretic Measurements.

Equation (8) gives the conditions under which a determination of the absolute velocities of ions will be satisfactory. A discussion of these conditions is more important in the study of cataphoretic velocities of colloidal particles as in contrast to electrolytic ions the boundary method constitutes the most useful method available.

The methods based on the analogy of Hittorf's measurements of transport numbers are evidently unsatisfactory. From the equations of Kohlrausch as also from the preceding discussion it is not difficult to show that in colloids containing electric carriers (including eletrolytic ions) of the same sign of different mobilities the condtions at different places of the colloidal solution cannot remain constant and the changes in concentration of the carriers of different categories that must result from the conduction of electricity will give us an average effect and not an absolute value of transport numbers. A physical interpretation of the data is not possible unless one knows the concentrations and mobilities of the carriers of electricity contained in the liquid. The extact interpretation will be very complicated. Even assuming that the concentration is uniform to begin with and that the products of electrolysis do not enter the colloidal solution changes in the relative concentrations of the charged particles are bound to occur on the passage of the current. This method rests on the integral effect of the current and it has been pointed out by Weber that it has not so far been possible to solve the integral effect in terms of the known factors, namely, the concentrations and mobilities of the different carriers. This method is only applicable in the case of simple colloids containing, say for example, carriers of any one sign having not more than one value for their mobility. Even then the values obtained by this method, being merely the integral changes in concentration on the passage of a current, requires a knowledge of the composition of the carriers for their interpretation in terms of the actual mobilities. An instance of the difficulties may be cited. For mixed solutions of the simple electrolytes AR and BR such that A and B have identical mobilities Kohlrausch shows that provided that to start with the concentrations of the ions are not constant all through the liquid, all that his differential equation implies is that the sum of the concentrations of A and B will remain unchanged on the passage of the current at any point but the ratio of their concen-

trations will change and Weber has shown that the integral effect admits of more than one solution, even if the direction of the current remains unchanged. There will be a change in the ratio of the concentrations of A to B and the transport numbers will appear to be different though we have started from the premise that the two have the same mobilities and, as they have a common ion, also the same transport numbers.

The moving boundary methods as usually used in cataphoretic measurements follow the procedure used by Burton (*Phil. Mag.*, 1906, vi, **1**, 425 ; compare also Galecki, *Z. anorg. Chem.*, 1912, **74**, 174 ; Pauli, Hofmeisters Beitrage, *Z. phys. Chem. u. Path.* 1906, **7**, 531 ; Michaelis, *Koll. Zeit.*, 1924, **34**, 326; Powis, *Z. physikal. Chem.*, 1925, **89**, 91). Burton's procedure sometimes yields results which vary as much as 300%. As a result of an investigation into the sources of error the writer has developed a procedure (*Proc. Roy. Soc.*, 1923, **103A**, 102 ; see also Freundlich and Zeh, *Zeit. physikal. Chem.*, 1925, **114**, 84 ; Kruyt and Willigen, *Zeit. physikal. Chem.*, 1927, **130**, 170 ; also *Koll. Zeit.*, 1928, **44**, 82) which obviates the difficulties arising out of a failure to consider the boundary conditions. The improvement consists in finding out an electrolyte which does not disturb the initial uniform potential gradient in the liquid and in directly measuring the potential gradients in different layers before and after the passage of the current. Colloidal arsenious sulphide particles carry with them mobile hydrogen ions. The boundary can only be stable when the upper layer in the U-tube is a dilute solution or a strong acid with an anion which moves faster than the negatively charged colloidal particle. It was found, however, that no noticeable adjustment takes place at the boundary (*loc. cit.* pp. 118-119) and a substitution of hydrochloric acid by sulphuric acid having the same specific conductivity as the colloid did not alter the rate of migration to an extent greater than the limits of experimental error. It has also been observed that under these conditions, the same cataphoretic speed is obtained (within the limits of experimental error) whether the slower moving carriers follow the faster moving ones or *vice versa*, though under most suitable conditions, it is possible to get results reproducible within 1%.

Colloidal particles settle on account of the difference between their density and that of the dispersion means. It is necessary in these cases to observe the cataphoretic speeds with both

rising and descending boundaries, in order to eliminate the speed of settling.*

As the result of a large number of measurements in the past few years, it has been found desirable to secure what may be termed '*an identical ionic environment*' (Chaudhury and Raichaudhuri, *J. Indian Chem. Soc.*, 1927, **4**, 498) during the movement of the colloidal particle and irrespective of the direction of the current.

The conditions for securing such an ionic environment can be understood in the light of Equation (8). The measurement of the cataphoretic velocity is obviously analogous to the measurement of the absolute velocity of an ion. With colloidal solutions of arsenious sulphide containing hydrogen ions in the mobile sheet of the double layer on account of the high mobility of the hydrogen ion, the disturbing effect given by Equation (8) will be negligile and any strong acid of same specific conductivity as the colloidal solution will secure uniform ionic environment, and the same speed will be observed both for rising and descending boundaries. The difficulties with a rising boundary pointed out by MacInnes (*loc. cit.* 1927) and considered by him to be due to irregular heating effects of the current do not occur as condition (5) laid down by Steele is satisfied. The particles are moving in a uniform ionic environment which is not materially affected by the direction of the current and it is immaterial whether the faster moving ion follows the slower moving ion or *vice versa*. As the hydrogen ions are the only carriers of positive electricity and the colloidal particles are the only carriers of negative electricity possessing the same mobility this colloid presents little difficulties in securing an 'identical ionic environment.'

On the other hand colloids such as ferric hydroxide presents considerable obstacles and require a detailed study of the nature of the carriers of electricity in order to secure a uniform ionic environment. Simplifications of our procedure as used by Freundlich (*loc. cit.*) and Kruyt (*loc. cit.*) are possible when these conditions have been determined from a preliminary study which can easily be carried out by our method. The use of the ultrafiltrate as the upper liquid does not always offer a way out as it is not free from objections (V. Gazzi. *British Chemical Abstracts, A.*, 1928, April, 359).

* It appears that the phenomenon which is commonly known as "barophoresis" is more complicated than is generally supposed to be.

Our observations with a ferric hydroxide sol which will be published shortly are of interest as illustrating what determines a uniform ionic environment. They show clearly that a dilute mixed solution of ferric and hydrogen chlorides of a definite composition is the most suitable for measurement of cataphoretic velocity. Chemical considerations point out that this should be so as the ferric hydroxide hydrosol which has been used in the above investigation contain free ferric and hydrogen ions.

It is generally implied in discussions on measurements of transport numbers by the moving boundary method that the slower moving ion adjusts its concentrations so as to secure a stable boundary such that both ions move with the same speed (compare Abegg and Gauss, *loc. cit.* ; MacInnes, *loc. cit.*). In that event it is impossible to measure correctly the cataphoretic speed of colloidal particles by the usual methods used for this purpose, as it does not take into consideration any such adjustment. Even if we take note of such an adjustment it is not possible to utilise this for a colloid of the type of ferric hydroxide sol containing carriers of positive electricity having *several* mobilities.

From the foregoing we conclude that the theoretical basis of methods of measurement of cataphoretic speed must rest on securing a 'uniform ionic environment' during the movement of the colloidal particles.

In conclusion we would refer to the bearing of the foregoing discussion on the theories and measurements of liquid junction potentials, which we intend to discuss in future in the light of experiments in progress in this laboratory.

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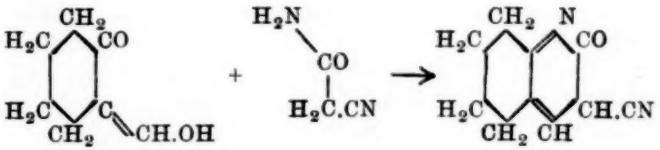
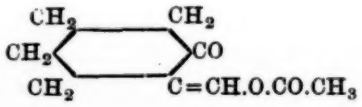
Alkylation of Hydroxymethylene*cyclo*hexanones.

By Hemendra Kumar Sen and Kanailal Mondal.

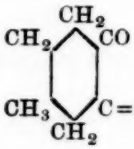
In a system containing a conjugated double bond of the type $O=\dot{C}-\dot{C}=\overset{1}{C}R$, the ethylenic linkage is generally found to be more reactive than the carbonyl (Harries and Lellmann, *Ber.*, 1897, **30**, 230, 2726; Harries and Jablonski, *Ber.*, 1898, **30**, 1370; Vorländer, *Ber.*, 1894, **27**, 2053; *Annalen*, 1897, **294**, 273; Lapworth, *J. Chem. Soc.*, 1904, **85**, 1214; Knoevenagel, *Ber.*, 1904, **37**, 4464). On condensing hydroxymethylene *cyclo*hexanones with cyanacetamide, quinoline derivatives are obtained (Sen Gupta, *J. Chem. Soc.*, 1915, **107**, 1347). From this the conclusion is drawn that the methylene group of cyanacetamide is more reactive towards the ethylenic than the ketonic bond of the hydroxymethylene ketone, the reaction being supposed to take place in the following way:



The suggestion that quinoline and not *iso*quinoline derivatives are to be expected owing to the aldehydic nature of hydroxymethylene *cyclo*ketones, does not appear to be probable as the reactivity of a β-diketone with cyanacetamide tends to disappear where the chance of enolisation is small (Sen and Basu, *J. Indian Chem. Soc.*, 1927, **4**, 51) and that identical quinoline derivatives are obtained from hydroxymethylene*cyclo*hexanone and its acetate—



Our original idea was to prepare the *O*-alkyl ethers of hydroxymethylene *cyclo*hexanones.



(R = an alkyl group).

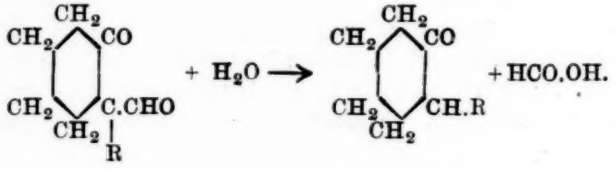
and condense them with cyanacetamide with a view to obtain quinoline derivatives, and thus adduce fresh evidence in support of the original hypothesis.

The alkyl ethers are usually formed by the action of alkyl iodides on the sodium salt of hydroxymethylene compounds

$$RCOCH:CHONa + R'I \longrightarrow RCOCH \cdot CHOR'.$$

Claisen prepared the ethyl ether of hydroxy-methylene camphor in this manner (*Chem. Centr.*, 1890, *ii*, 878). The ethers undergo hydrolysis and regenerate original ketones, rupture taking place at the double bond.

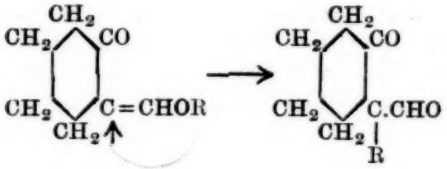
Contrary to our expectation, it was found that the reaction did not proceed in this manner with hydroxymethylene*cyclo*hexanones. For, when alkyl iodides were allowed to react with their sodium salts, the products on hydrolysis did not yield the original ketones from which the hydroxymethylene compounds were derived, but instead, new ketones were obtained in which alkyl substitution in the *ortho*- position to the ketonic group had taken place. As these ketones were often unmixed with the original ketones, it could be held that *O*-alkyl ethers were not being generally formed. Evidently the products were mainly *C*-alkyl ethers which alone could give alkylated ketones on hydrolysis of the formyl group.



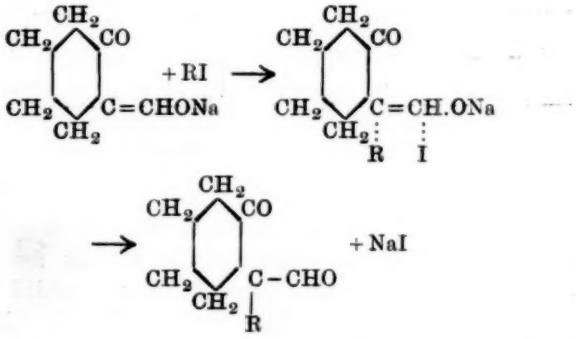
That the first product formed by the interaction of the Na-salt of hydroxymethylene*cyclo*hexanone with an alkyl iodide is a substituted keto-aldehyde is shown by the reduction of ammoniacal silver nitrate and copper salt solutions. This behaviour of the

hydroxymethylene compound is very different from the ordinary and can be explained by assuming:

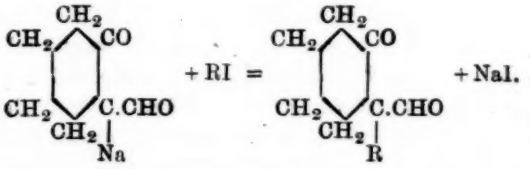
(I) The wandering of an alkyl group from oxygen to carbon after the formation of the *O*-ether.



(II) An addition reaction followed by separation of sodium iodide such as Michael assumes in explaining the formation of *C*-derivatives from the sodium compound of acetoacetic ester and alkyl iodides (*J. pr. Chem.*, 1888, (*ii*)**37**, 473).

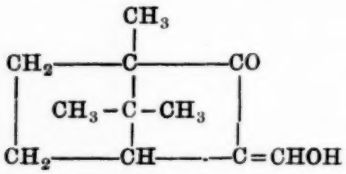


(III) By assuming an aldehydic structure for the sodium compound when direct substitution of Na by an alkyl group takes place.

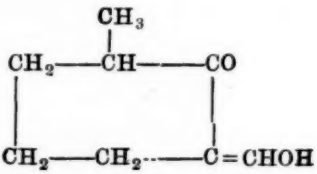


Assumption (I) does not appear to be probable. The formation of the *C*-compound takes place even in the cold and without the use of a reagent which is known to produce isomeric change under

the condition. Similar *O*-alkyl compounds like the ethyl ether of hydroxymethylenecamphor do not appear to be so unstable. Again such an assumption does not find favour in explaining the formation of *C*-derivatives of acetoacetic ester. Regarding (II) it may be seen that it does not satisfactorily explain the two different types of reactions as represented by the formation of *O*-ethers in certain cases and *C*-derivatives in others. If it is assumed that addition reactions take place in the latter and substitution in the former and that the nature of the reaction (addition or substitution) is determined by Michael's negative positive rule, it cannot be imagined why any difference should be observed, for instance, between hydroxymethylenecamphor and hydroxymethylene*ortho*-methyl*cyclo*hexanone both of which possess similar structures but yield different kinds of alkyl compounds.



Hydroxymethylene camphor.



Hydroxymethylene-*o*-methyl-*cyclo*hexanone.

As regards (III) there is admittedly a great difficulty in giving an aldehydic structure to the sodium salt, as, in the first place, hydroxymethylene ketones have generally been regarded as pure enolic compounds (Claisen, *Chem. Centr.*, 1890, (*ii*), 878; von Pechmann, *Ber.*, 1892, **25**, 1040). Claisen, in fact, distinguishes them from β-diketones, as, according to him, only *O*-derivatives can be obtained from the sodium compounds of the former (which is however not a fact as seen in the present case) whereas those of the latter can give *C*-derivatives (*Ber.*, 1892, **25**, 1776). The existence of the aldehydo form in the free hydroxymethylene compound, which must be a condition that the aldehydic sodium compound may exist, does not appear to have been established before. W. Wislicenus considered α and β forms of the methyl and ethyl esters of formyl phenyl acetic acid (other forms obtained he regarded as mixtures) as keto and enol modifications at first but after reviewing all evidence for thirty years he is now inclined to the belief that they are *cis*- and *trans*-enol forms both of which rapidly absorb a molecule of bromine and are

equally soluble in alkali solution (*Annalen*, 1896, **291**, 147; 1900, **312**, 62; 1912, **389**, 270; 1916, **413**, 206; *Ber.*, 1899, **32**, 2837; Michael, *Annalen*, 1912, **391**, 235, 215; 1914, **406**, 137; Meyer, *Ber.*, 1912, **45**, 2863; Dieckmann, *Ber.*, 1916, **49**, 2213). Dieckmann also holds the same view (*Ber.*, 1917, **50**, 1357). Recent absorption spectra method supports the same conclusion (*J. Chem. Soc.*, 1927, **131**, 713). K. H. Meyer's bromine titration method, applied to few hydroxymethylene ketones by some investigators, shows them to be enolic compounds.

As no alternative to (III) could be thought of, it was necessary to determine whether the hydroxymethylene compounds under investigation were really pure enols or mixtures of *keto* and *enol* phases. The matter was settled by directly determining the percentage of enol in them. Applying Meyer's method some were found to contain a fairly large porportion of the keto form. Hydroxymethylene*ortho*methyl*cyclo*hexanone, for example, contains about 54% and hydroxymethylene-*meta*-methyl*cyclo*hexanone about 40% of the keto form. Their behaviour was also found to be exactly analogous to the other class of substances which show keto-enol tautomerism, so far as the effect of solvent, temperature and concentration on the equilibrium is concerned.

It has been determined by different observers both by chemical and physical methods that dissociating solvents like alcohol rapidly ketonises the enol and, whereas the equilibrium is shifted towards the keto side in such media, it is shifted towards the enol in solvents like benzene and that dilution in the same solvent always increases the proportion of the enol form (Wislicenus, *Ber.*, 1899, **32**, 2837; Brühl, *Ber.*, 1899, **32**, 2326; K. H. Meyer, *Annalen*, 1911, **380**, 212; *Ber.*, 1910, **43**, 3044).

Hantzsch (*loc. cit.*), by absorption spectra method, finds that the equilibrium is shifted towards the enol side by the rise of temperature. Meyer on the other hand, after studying a number of compounds, concludes that the keto form is favoured by the rise of temperature (*Annalen*, 1911, **380**, 212; *Ber.*, 1914, **47**, 833).

The rapid ketonising effect of alcoholic solution was observed in all the cases we have examined (*vide* Experimental). Similar effect has been noticed by Meyer in the case of ethyl acetoacetate (*Annalen*, 1911, **380**, 212).

The enolising effect of benzene and more so of ether was observed with hydroxymethylene-*p*-methyl*cyclo*hexanone. Alcohol, ether

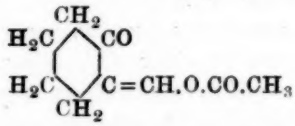
and benzene as solvents all showed approximately 77 per cent. of enol on the first day. After a week 50 per cent. of enol was observed in alcoholic solution whereas the enolic value rose to 93 per cent. in benzene and 97 per cent. in ether. Meyer, with acetoacetic ester, finds a higher percentage of enol in ether than in benzene (*Annalen*, 1911, **380**, 212) but the observation of Wislicenus appears to be in the opposite direction. Regarding the effect of concentration, dilution was noticed to show increased enolic percentage though the effect was not much marked. A 0·47 per cent. solution of hydroxymethylene-*p*-methyl*cyclo*hexanone in alcohol showed 87 per cent. of enol, whilst an 1·32 per cent. solution in the same solvent showed only 80 per cent. of enol after the same interval from the time of preparing the solutions. Hydroxymethylenecamphor practically contains 100 per cent. of enol. Other compounds examined showed similar results (*vide* Experimental).

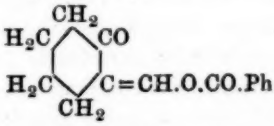
These results leave no doubt as to the possibility of the existence of the keto form in the hydroxymethylene compound and consequently of the aldehydic sodium compound. Nef's assumption that sodium in carbonyl compounds is never directly attached to carbon is disproved (Brühl, *Ber.*, 1892, **25**, 366). Though an enolic formula is usually given to the sodium compound of tautomeric substances, the most satisfactory explanation as suiting the most varied condition is that supplied by Lapworth (*J. Chem. Soc.*, 1912, **101**, 1508) in which there is an equilibrium established between the dissociated ions of the two metallic derivatives or in other words, an equilibrium mixture of both metallic compounds is present. The equilibrium of the sodium compound of acetoacetic ester is represented as

$$CH_3.\overset{|}{C}O=CH.CO_2C_2H_5 + Na' \overset{\rightarrow}{\leftarrow} CH_3.CO.\overset{|}{C}H.CO_2C_2H_5 + Na'$$

which is equivalent to the presence of two sodium compounds $CH_3.C(ONa):CHCOOC_2H_5$ and $CH_3.CO.CHNa.COOC_2H_5$. The equilibrium may shift from the one side to the other according to the conditions of the reaction or nature of the reagent or both. In our case, it may be assumed that the alkyl iodide reacts with the sodium compound of one form only, either the enolic or the aldehydic, both of which exist in equilibrium. The exclusive formation of one kind can be easily explained.

It may be mentioned in this connection that the action of acetyl chloride and benzoyl chloride proceeds in these cases in the usual way, *i.e.*, the acetates and benzoates of the following formulae are





formed by simple substitution of the enolic sodium compound. This is in accordance with Lapworth's view. The conception of equilibrium between metallic derivatives therefore finds an important confirmation in the above reactions which can then be satisfactorily explained on the simple substitution principle.

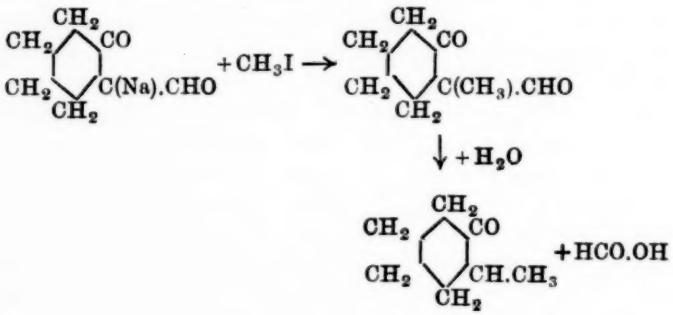
As already mentioned, the *C*-alkyl ethers undergo hydrolysis and alkylated ketones result. The reaction is found to be general with *cyclo*hexanone and the different substituted *cyclo*hexanones if only one *ortho*-position is free to yield hydroxymethylene derivatives. Indeed, the method can be used for general synthetical preparations of *ortho*-alkylated ketones. By using sodium salts and different alkyl iodides, methyl, ethyl, *iso*propyl and benzyl radicals have been introduced into the nuclei of different *cyclo*-ketones in *ortho*-position to the ketonic group. Thus *cyclo*hexanone gives a mono-substituted, and mono- and di-alkyl ketones give di- and tri-alkyl ketones respectively. The mono alkyl compounds obtained from hydroxymethylene*cyclo*hexanone in alcoholic solution, sodium ethoxide and an alkyl iodide or from the sodium salt in benzene or ether suspension and an alkyl iodide, are pure and obtained in good yield.

The dialkyl compounds obtained from mono-alkyl ketones is obtained as mixtures of the two in alcoholic solution which can however be separated ; but pure products may be obtained by using the dry sodium salt in ether or benzene suspension. The reaction product may be easily identified on the following basis :

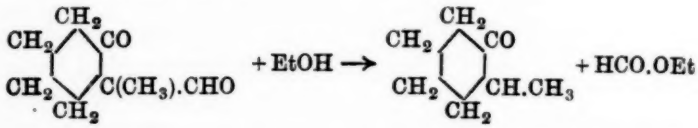
On distilling the alkylated product with alkali solution, any free hydroxymethyleneketone or its *O*-derivative yields the original ketone and the *ortho*-alkyl derivatives. Thus the hydrolysed product in all cases will be either the original ketone, or the substituted ketone, or a mixture of the two. Instances of all these have been noticed in carrying out the reaction in alcoholic solution. *cyclo*Hexanone in this way produces pure *o*-methyl*cyclo*hexanone, the three methyl compounds give mixtures, whereas the original ketone is obtained

when acetophenone is used, an *O*-alkyl compound being the only methylation product in the last case. The products can be mostly identified by comparison with the known ketones specially in the form of their derivatives (oximes or semicarbazones).

When the sodium salt of hydroxymethylene*cyclo*hexanone is heated with methyl iodide in dry benzene, a thick oil is obtained which distils with decomposition. The liquid reduces alkaline copper and silver salt solutions and does not form a semicarbazone easily which it readily yields on addition of dilute caustic soda solution or on distilling with it. The semicarbazone melts at 192° which shows no lowering when mixed with the semicarbazone prepared from a sample of pure *o*-methyl*cyclo*hexanone. The hydrolysed liquid itself has the characteristic smell of *o*-methyl*cyclo*hexanone and has the same boiling point. The reaction may be represented as follows:



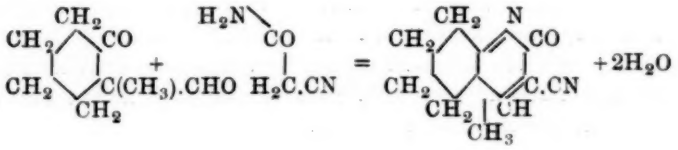
It is interesting to note that when hydroxymethylene*cyclo*hexanone is heated with sodium ethoxide and methyl iodide in alcoholic solution in a pressure bottle, the entire product is at once *ortho*-methyl*cyclo*hexanone. We may assume that the *C*-methyl ether which is first formed, is decomposed by alcoholic alkali to *O*-methyl *cyclo*hexanone.



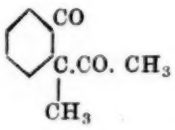
On the other hand, carrying on this reaction under reflux, two fractions are obtained. The lower fraction is *o*-methyl*cyclo*hexanone and the higher fraction on removal of the little free hydroxy-

methylene*cyclo*hexanone it contains, yields *o*-methyl*cyclo*hexanone on treatment with dilute caustic soda solution. The higher fraction probably contains the undecomposed *C*-methyl ether as the proportion of the lower fraction increases and that of the higher decreases on longer heating. Pure *o*-methyl*cyclo*hexanone is also obtained from the Na-salt taken in ether and treated in the cold with methyl iodide. Thus it appears, the sodium salt could not be made to produce any *O*-methyl ether under any of the conditions mentioned which, if produced, must have been in very small quantities, as, otherwise, it would have contaminated the final product with *cyclo*hexanone. There is reason to believe, however, that such alkylations do not always proceed to completion depending on the solvent and the temperature used, accounting thereby for the comparatively lower yields of synthesised alkyl ketones.

An attempt was made to bring about the condensation of the *C*-methyl ether with cyanacetamide as it would throw some light on the question whether the condensation of the latter substance with free hydroxymethylene*cyclo*hexanone was taking place in its enolic or aldehydic phase. If the latter, the β-keto-aldehyde used would give rise to a quinoline derivative, thus:



But as no condensation (Michael or Knoevenagel) occurred, one would be inclined to think that condensation of the hydroxymethylene ketone occurs in its enolic phase. Sen and Basu similarly failed to obtain any condensation product from methyl acetyl *cyclo*hexanone

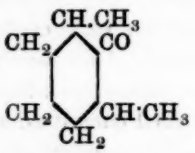


and cyanacetamide (*loc. cit.*). There also the difficulty of enolisation probably hindered condensation.

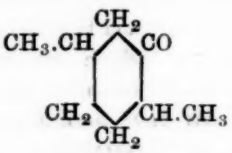
But the fact that the formyl group of the *C*-methyl ether is readily split off must not be lost sight of. The compound might

have got decomposed before any condensation with cyanacetamide could occur.

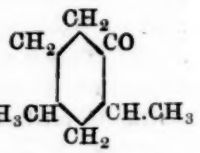
It has already been mentioned that each of the *o*-, *m*-, and *p*-methyl *cyclo*hexanones gives a dimethyl ketone.



2: 6-Dimethyl from *ortho*.



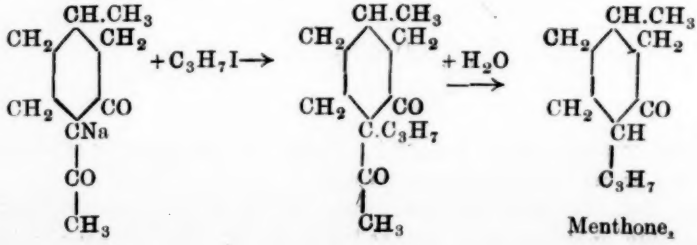
2: 5-Dimethyl from *meta*.



2: 4 Dimethyl from *para*.

Whereas the product is a pure dimethyl ketone when ether or benzene is used with the sodium salt, hydroxymethylene mono methyl ketone in alcoholic solution in the presence of sodium ethoxide produces a mixture of a mono-and a di-methyl ketone, the latter however being invariably in excess of the other. It appears, therefore, that the possibility of *O*-alkyl ethers or the hydroxymethylene ketone itself being hydrolysed to the original ketone cannot be altogether ignored. The case of hydroxymethelene *cyclo*hexanone itself is different from other homologues, as the former yields alkylated ketone whether in ether, benzene, or alcoholic medium, whereas the latter namely homologues of hydroxymethylene *cyclo*hexanone give a mixture of alkylated ketone and the original ketone in alcoholic solution.

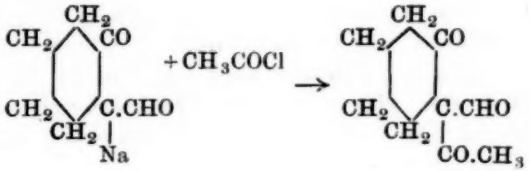
From the feregoing reactions as also from the analogy which the hydroxymethylene ketones are found to bear to acetyl *cyclo*ketones it could be seen that menthone could be synthesised from hydroxymethylene-*m*-methyl*cyclo*hexanone and *iso*propyl iodide after the manner of its production from 2-acetyl-5-methyl*cyclo*hexanone in presence of sodium ethoxide.



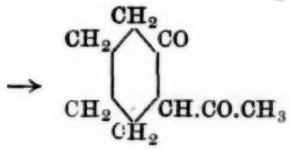
Menthone.

It would also be expected from what has already been noticed that in alcoholic solution, a mixture of *m*-methyl*cyclo*hexanone and menthone would be obtained. The expectation was justified by the results obtained. The hydrolysed product was a liquid from which the smell of menthone could be perceived. The semicarbazone obtained from this liquid was impure and repeated crystallisation gave no pure product but the oxime prepared from the mixture which melted at 78°, on crystallising once from alcohol, melted at 83° and on second crystallisation from the same solvent, melted fairly sharp at 92°. The oxime thus obtained was shining crystals but the yield was small. The melting point of the oxime of inactive menthone is differently given as 78-82° and 98-99°.

That the reaction of the sodium salt of the hydroxymethylene ketone with acetyl chloride did not produce a *C*-derivative (I) or (II) after the following fashion :

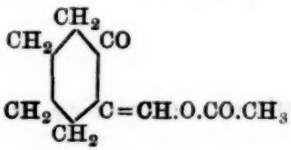


I



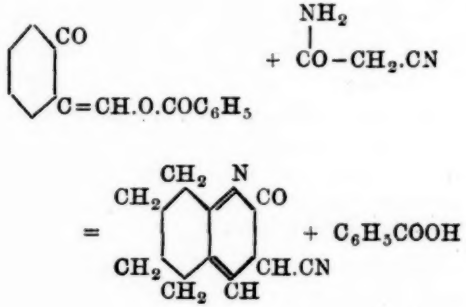
II

but an acetate of the following formula



appeared from the following considerations. The thick liquid that was obtained by ether extraction after treating the sodium salt of hydroxymethylene*cyclo*hexanone in ether suspension with acetyl chloride was treated with dilute alkali. If the first reaction took

place, acetyl *cyclo*hexanone was most likely to be obtained after the last operation. But the liquid was not found to possess the properties of the latter. The thick liquid had the acetate-like smell quite unlike that of acetyl *cyclo*hexanone. Besides it did not give any immediate colouration with alcoholic ferric chloride. Acetyl *cyclo*hexanone (a β-diketone) at once develops violet colouration with alcoholic ferric chloride solution. The slow appearance of colour in the acetylated compound, which also appeared on warming, may be attributed to hydrolysis and change into the hydroxymethylene ketone. The formula for the acetate was confirmed by analysis of the semicarbazone which was quickly formed from the liquid. Mention has already been made of this acetate which was obtained by the action of acetic anhydride on hydroxymethylene *cyclo*hexanone and its condensation with cyanacetamide. The action of benzoyl chloride is similar to the above. By the same series of arguments the solids prepared are proved to be benzoates which like the acetates readily form semicarbazones and appear to give quinoline condensation products with cyanacetamide. The smell of ethyl benzoate is distinctly perceptible when the benzoate and cyanacetamide are treated with sodium ethoxide in alcoholic solution. The condensation product may be supposed to be formed according to the following scheme:—



The Na-salt of hydroxymethylene acetophenone does not give anything like propiophenone with methyl iodide or butyrophenone with ethyl iodide. Its reaction appears to be similar to that of the sodium compound of hydroxymethylene camphor though one is an open-chain ketone and the other a cyclic compound. Liquid products which are obtained rapidly absorb bromine and yield pure aceto-

phenone on hydrolysis. They are, therefore, *O*-ethers. Ethoxy methylene acetophenone gave a condensation product with cyanacetamide which melted above 280°. The yield being small, the nature of the reaction could not be investigated.

Experimental.

*Action of Methyl Iodide on the Sodium Salt of Hydroxymethylene-*cyclo*hexanone in Benzene Suspension.*

To hydroxymethylene *cyclo*hexanone (20 g.) in 150 c.c. of dry benzene the requisite quantity of metallic sodium (wire) was added. The mixture was heated on the water-bath at 100° when the metal began slowly to react as indicated by the evolution of hydrogen. The superficial incrustration of the sodium salt was broken up from time to time to expose fresh surface and the heating was continued for 18 hours. The sodium salt thus obtained was a bulky granular powder. It was introduced together with benzene into a pressure bottle and heated for 12 hours at 100° with three times the required quantity of methyl iodide. After cooling, the precipitate of sodium iodide was filtered off and the benzene solution of the reaction product distilled under ordinary pressure to get rid of benzene. The residual liquid was distilled under reduced pressure, when it distilled with slight decomposition. At 130-150°/45 mm. a coloured distillate (10 g.) was obtained. This liquid reduced Fehling's solution (when heated with or without the addition of alcohol) or ammoniacal silver nitrate. The liquid however did not readily form a semicarbazone which however at once appeared on the addition of dilute caustic soda solution. This semicarbazone was found to be identical with that of *o*-methyl*cyclo*hexanone (m.p. 191°-92°).

*Hydrolysis of the above Liquid: Formation of 2-Methyl*cyclo*hexanone.*

The liquid was distilled with dilute caustic soda solution. The distillate was extracted with ether. It had the characteristic smell of *o*-methyl*cyclo*hexanone, and gave a semicarbazone which appeared as shining crystals from alcohol. The semicarbazone melted at 192°. It showed no lowering of m.p. when it was mixed

with the semicarbazone of *o*-methyl*cyclo*hexanone which latter also melted at 192°. (Found: N, 25·01. $C_8H_{15}ON_3$ requires N, 24·85 per cent.).

*Action of Methyl Iodide on Hydroxymethylene*cyclo*hexanone in Alcoholic Solution in Presence of Sodium Ethoxide under Pressure.*

Hydroxymethylene*cyclo*hexanone (25 g.) was dissolved in alcohol (70 c.c.), sodium (4·6 g. dissolved in 100 c.c. of alcohol) was added to it. The solution which contained the sodium salt of hydroxymethylene *cyclo*hexanone was heated on the water-bath with about three times the requisite amount of methyl iodide (70 g.) in a pressure bottle till neutral (6 hours). The excess of methyl iodide and alcohol were distilled off from sand-bath and water was added to the residue and its ether extract taken. It was dried over anhydrous sodium sulphate and on expelling the ether from water-bath, the residual liquid was distilled under reduced pressure (yield, 14 g.); b.p. 86°-88°/49 mm. The liquid boiled at 164-166° under ordinary pressure. The semicarbazone prepared from the liquid came down in beautiful caystals, m. p. 189°. A mixture of this semicarbazone with that of *o*-methyl*cyclo*hexanone showed no lowering. The semicarbazone was obtained in still purer condition melting at 192° by removing the traces of contaminating free hydroxymethylene *cyclo*hexanone from the liquid by washing it with dilute alkali solution and finally distilling it with the same. Apart from the smell of the liquid which is sufficient to characterise it as *o*-methyl*cyclo*hexanone, the comparison of the semicarbazone with that of a known sample of *o*-methyl*cyclo*hexanone and the analysis of the semicarbazone, established the liquid to be *o*-methyl*cyclo*hexanone.

The above Experiment carried out under Reflux.

On conducting the experiment under reflux two fractions were obtained. The lower fraction (10 g.) boild at 93-98°/ 52 mm. which was identified as *o*-methyl*cyclo*hexanone containing a small amount of unaltered the hydroxymethylene compound. The higher fraction collected between 110° and 130° was redistilled but no steady boiling point was obtained. The hydroxymethylene ketone was removed from the liquid by treatment with dilute sodium carbonate solution as the soluble sodium salt. The liquid was distilled with dilute

caustic soda solution and the distillate was pure *o*-methyl*cyclo*hexanone as was shown by its semicarbazone.

Action of Methyl Iodide on the Sodium Salt of Hydroxymethylene cyclo*hexanone in Ether Suspension in the Cold.*

Ten gms. of the sodium salt thoroughly washed with dry ether were mixed with an excess of methyiodide in a closed vessel which was shaken from time to time. After about a week the contents were filtered and the ether was removed in vacuum. Two gms. of a liquid were obtatned which gave *o*-methyl-*cyclo*hexanone on treatment with dilute NaOH solution. It was considered pure as its semicarbazone melted sharp at 192°.

*Action of Ethyl Iodide on Hydroxymethylene*cyclo*hexanone.*

Ten gms. of a colourless liquid were obtained from 20 gms. of hydroxymethylene *cyclo*hexanone when the latter was heated with the required amount of sodium ethoxide, alcohol and ethyl iodide. The liquid distilled at 125-135°/10 mm. On a second distillation, a fraction was collected which boiled at 130-132°/10 mm. After treating it in the usual way to remove hydroxymethylene *cyclo*hexanone, the presence of which was detected by the ferric chloride reaction, and hydrolysing the liquid, a semicarbozane was prepared. It was crystallised from alcohol ; m. p. 157°. The semicarbazone of ethyl *cyclo*hexanone is known to melt at 157°. (Found : N, 23·1. $C_9H_{17}ON_3$ requires N, 22·9 per cent.).

Action of Methyl Iodide on Hydroxymethylene-o-methyl cyclo*hexanone.*

Conducting the experiment in alcoholic solution in presence of sodium ethoxide in a closed bottle and proceeding as before 15 gms. of a liquid having peppermint-like odour were collected (using 25 gms. of the hydroxymethylene compound). The liquid distilled at 170-200° under ordinary pressure but the greater portion of it boiled at 175-180°. The whole of the liquid was distilled with 20% caustic soda solution. The oil was extracted from the distillate with ether. The semicarbazone prepared from the colourless liquid melted completely at 183°. It was impure and analysis showed about 24% of nitrogen. As the semicarbazone of the monomethyl ketone contains 25% nitrogen and that of the dimethyl ketone 23%, the liquid appeared to be a mixture of nearly equal quantities of *o*-methyl*cyclo*hexanone and the dimethyl compound derived from

it. An oxime was prepared from it by the following method. Three gms. of the liquid were dissolved in methyl alcohol. A slight excess of hydroxylamine hydrochloride with four times the theoretical amount of caustic soda solution was added to the solution and heated for half an hour on the water-bath. The whole was allowed to evaporate spontaneously in air when the oxime crystallised out slowly. On recrystallisation from methyl alcohol it melted at 118°. This corresponded to the oxime of 2: 6-dimethyl*cyclo*hexanone. (Found: N, 10·35. $C_8H_{15}ON$ requires N, 10·0 per cent.).

By conducting the methylation under reflux and in alcoholic solution, 16 gms. of 2-methyl hydroxymethylene *cyclo*hexanone gave 16 gms. of the methylated product boiling at 110-150/ 40 mm. On fractionation, two equal fractions were collected—one boiling at 120-130/30 mm. and the other at 130-135/30 mm. On hydrolysing both fractions with 20% NaOH, and treating the steam distilled product with hydroxylamine, an oxime melting at 118° was obtained. This corresponded to the oxime of 2: 6-dimethyl*cyclo*hexanone.

Action of Methyl Iodide on the Sodium Salt of Hydroxymethylene o-*methyl*cyclo*hexanone in Benzene Suspension.*

A small yield of the dimethyl compound was obtained in a manner described in the first experiment. That the dimethyl componnd was formed appeared from the peppermint-like odour of the liquid which is distinct from that of *o*-methyl*cyclo*hexanone. That the liquid was a very nearly pure dimethyl ketone was proved by preparing its semicarbazone which formed fine crystals (from alcohol) and melted at 193-194°. The mixture of this semicarbazone with that of *o*-methyl*cyclo*hexanone melted at 178°. (Found : N, 23·4. $C_9H_{17}ON_3$ requires N, 23·00 per cent.).

Action of Methyl Iodide on the Sodium Salt of Hydroxymethylene-m-*methyl*cyclo*hexanone.*

The sodium salt of hydroxymethylene *m*-methyl-*cyclo*hexanone was suspended in ether and was kept at room temperature in contact with methyl iodide. After several days, the dimethyl compound having the smell of the above dimethyl ketone was obtained by hydrolysing the resultant liquid. Its semicarbazone melted at 176°. The semicarbazone of 2:5-dimethyl*cyclo*hexanone is known to melt at 176°.

A mixture of this semicarbazone with that of *m*-methyl-*cyclo*hexanone melted at 150-155°. The semicarbazone was pure. (Found: N, 23·25. $C_9H_{17}ON_3$ requires N, 23 per cent.).

Action of Methyl Iodide on Hydroxymethylene-p-methylcyclohexanone in Alcoholic Solution with Methyl Iodide and Sodium Ethoxide.

Proceeding in the usual way, an impure product having the same peppermint-like odour of the other two dimethyl ketones was obtained. The liquid (in alcohol) quickly gave an oxime when shaken with hydroxylamine hydrochloride and excess of concentrated caustic soda solution. On crystallising from alcohol the *oxime* came out in long colourless prismatic needles which melted at 96°. (Found: N, 10·01. $C_8H_{15}ON$ requires N, 10·0 per cent.).

Analysis of the semicarbazone prepared showed the methylated product to be a mixture of the mono-and the di-methyl ketone. (Found: N, 23·96. $C_9H_{17}ON_3$ requires N, 23 per cent.).

Action of Benzyl Iodide on Hydroxymethylene-o-methylcyclohexanone.—*2-Methyl-6-benzylcyclohexanone* was prepared from hydroxymethylene-*o*-methyl*cyclo*hexanone and benzyl iodide using alcohol and sodium ethoxide. The yield was small and the semicarbazone was impure. It melted at 140° sintering at 132°.

Menthone.—Hydroxymethylene-*m*-methyl*cyclo*hexanone (20 gms.) with *iso*propyl iodide (55 g.) and the requisite amount of sodium dissolved in alcohol were heated in a closed bottle for 6 hours. A colourless liquid (13 g.) distilling at 107-115°/40 mm. was collected and distilled with caustic soda solution. Menthone-like smell could be recognised in the distillate but the odour was not distinct as it was masked to a great extent by that of *m*-methyl-*cyclo*hexanone which could also be perceived. The oxime which was prepared from the liquid by the previous method melted at 73-78°. By crystallising it from alcohol the colourless oxime melted at 80-83°. After a second crystallisation from alcohol, fine colourless shining crystals that were obtained melted fairly sharp at 92°. Analysis showed a little higher percentage of N. Exactly simliar result was obtained by repeating the experiment. (Found: N, 8·8. $C_{10}H_{20}ON$ requires N, 8·3 per cent.).

The *semicarbazone* after crystallising once from alcohol melted completely at 120°, after another crystallisation at 128°. After

two more crystallisations, the m.p. rose to 145° but no pure product was obtained. This was analysed and from the percentage of N it contained, it was concluded that the hydrolysed liquid was a mixture of the two ketones which could only be present in the final product. (Found: N, 22·76. $C_{11}H_{21}ON_3$ requires N, 20·1 per cent. $C_8H_{15}ON_3$ requires N, 24·90 per cent.).

Action of Methyl Iodide on Hydroxymethylene-3:4-dimethyl cyclohexanone.

From the sodium salt and methyl iodide, 2:3:4-trimethyl-*cyclo*hexanone was obtained. Its *semicarbazone* melted at 212°. A mixture of this semicarbazone with that of the dimethyl ketone used for its preparation sintered at 190° and melted completely at 200°. The trimethyl ketone has the same smell as the dimethyl ketone. The semicarbazone of the dimethyl ketone melts at 190°. (Found: N, 21·5. $C_{11}H_{19}ON_3$ requires N, 21·35 per cent.).

Action of Acetyl Chloride on the Sodium Salt of Hydroxymethylene cyclo*hexanone.*

Ten gms. of sodium salt were suspended in ether and an excess of acetyl chloride was gradually added to the sodium salt while it was kept cool in ice. Sodium chloride separated with stirring of the mixture. The product was extracted with ether and treated with dilute sodium carbonate solution. The viscous oil which was obtained from it was almost colourless, possessed the smell of an acetate and only slowly gave colouration with alcoholic ferric chloride. It readily formed a semicarbazone which was crystallised from alcohol; m.p. 182-184°. A mixture of this with the semicarbazone of *cyclo*hexanone melted at 155°. The liquid readily absorbed bromine and on hydrolysis yielded *cyclo*hexanone, the semicarbazone of which melted at 166°. (Found: N, 19·01. $C_{10}H_{14}O_3N_3$ requires N, 18·75 per cent.).

*Action of Acetyl Chloride on the Sodium Salt of Hydroxymethylene-*m*-methyl*cyclo*hexanone.*—The acetate was obtained as in the previous experiment in the form of a viscous oil. It had all the properties of the above acetate but did not readily form a semicarbazone.

*Action of Benzoyl Chloride on the Sodium Salt of Hydroxymethylene-*o*-methyl*cyclo*hexanone.*—To 50 gms. of the sodium salt of hydroxymethylene-*o*-methyl-*cyclo*hexanone in ether suspension, benzoyl chloride was gradually added. The mixture became

hot while sodium chloride separated. After the reaction was complete, which could be easily tested with $FeCl_3$, the mixture was treated with very dilute caustic soda solution. On extracting the mixture with ether and evaporating the ether, 10 gms. of a solid were obtained. This was crystallised from alcohol and melted at 85°. It is unstable and decomposes on keeping for several days. Its alcoholic solution does not give coloration with ferric chloride. The colour however appears on standing. It readily gave a semicarbazone, m. p. 175°. (Found: N, 14·2. $C_{16}H_{19}O_3N_3$ requires N, 13·95 per cent.).

Action of Benzoyl Chloride on the Sodium Salt of Hydroxymethylene-p-*methyl*cyclo*hexanone*.—Proceeding as above, a solid benzoate was obtained which melted at 95°. It had all the properties of the other benzoate. Its *semicarbazone* melted at 183-184°. (Found: N, 14·2. $C_{16}H_{19}O_3N_3$ requires N, 13·95 per cent.).

Action of Methyl Iodide on the Sodium Salt of Hydroxymethylene acetophenone.—The sodium salt of hydroxymethylene acetophenone (35 g.) was heated with methyl iodide and benzene for 12 hours. On removing benzene, a coloured liquid (8 gms.) with peculiar smell boiling at 120-130°/ 45 mm. was obtained which could not be obtained pure, as it decomposed on heating. The liquid readily absorbed bromine, did not form a semicarbazone quickly and on hydrolysis, yielded pure acetophenone. The semicarbazone of the hydrolysed product melted at 196-197°. Acetophenone semicarbazone also melted at the same temperature. A mixture of the two melted at 196°. The experiment was carried out in presence of alcohol when only acetophenone was obtained on hydrolysis. (Found: N, 23·6. $C_9H_{11}ON_3$ requires N, 23·7 per cent.).

Action of Ethyl Iodide on the Sodium Salt of Hydroxymethylene acetophenone.—The small quantity of a coloured liquid which was obtained by heating the sodium salt with ethyl iodide alone was found to yield acetophenone on hydrolysis. It gave a condensation product with cyanacetamide in presence of piperidine which melted with decomposition above 280°. It dissolved in caustic soda solution on warming. The yield was small.

Estimation of the Keto-Enol Quantities in the Hydroxymethylene Ketones.

Hydroxymethylene-m-*methyl*cyclo*hexanone*.—2·3575 Gms. of the pure compound were dissolved in 250 c.c. of alcohol. Freshly

prepared bromine solution in alcohol (N/10) was added to 10 c.c. of the above solution in slight excess so that the colour of bromine persisted in the liquid. The temperature was kept at —7° during the addition of bromine. β-Naphthol also dissolved in alcohol was immdiately added in order to remove the uncombined bromine. On the addition of potassium iodide solution, iodine was liberated. After warming for a minute the liberated iodine was titrated with standard thiosulphate solution. The following results were obtained:

	1st day.	After 12 days.	After 4 months.
P.c. of enol.....	62	41	13

*Hydroxymethylene*cyclo*hexanone* :—1·0865 Gm. of the substance were dissolved in 250 c.c. of alcohol. The following results were obtained.

	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.	7th day.	After 8 days.
P.c. of enol	87	77	67	66	66	66·5	66	67

On boiling with alcohol for 3 minutes—45% enol.

Hydroxymethylene-p-*methyl*cyclo*hexanone*.
(*In Alcohol*).

1·1730 Gms. of the substance dissolved in 250 c.c. of alcohol gave the following results.

P.c. of enol...	1st day. 87	2nd day. 80	3rd day. 68	7th day. 50	After 18 days. 40	After 3 months. 20

(*In Benzene*).

1.0940 Gms. dissolved in 250 c.c. of benzene showed the following results.

	1st day.	2nd day.	3rd day.	6th day.	After 7 days.
P.c. of enol...	85	86	93	93	93·5

(*In Ether*).

0·7500 Gm. was dissolved in 100 c.c. of ether and the following results were obtained.

	1st day.	2nd day.	3rd day.	7th day.
P.c. of enol ...	89	92	95	97

(*At Higher Concentration*).

1·3176 Gms. in 100 c.c. of alcohol showed 80% of enol on the 1st day and 70% the next day.

Hydroxymethylene Camphor.

0·2478 Gm. of hydroxymethylene camphor in 100 c.c. of alcohol.

	1st day.	2nd day.	3rd day.	4th day.
P.c. of enol...	98·4	92·85	87·12	81·75.

Hydroxymethyleneacetotoluone.

0·3435 Gm. of the substance dissolved in 100 c.c. of alcohol.

	1st day.	2nd day.	3rd day.	4th day.	5th day.
P.c. of enol...	96·2	79·6	61·5	60·3	42·7

Hydroxymethylene-3 : 4 -*methyl*cyclo*hexanone*.
(*In Alcohol*).

1·0146 Gms. of the substance were dissolves in 100 c.c. of alcohol.

1st day 78%
After a month 40%
On boiling with alcohol ... 52% (first day)

(*In Benzene*).

0·3156 Gm. was dissolved in 250 c.c. of benzene.

	1st day.	2nd day.	After a month.
P.c. of enol ...	82	86	86

1·3 Gms. in 100 c.c. of benzene gave 75% of enol in freshly prepared solution.

(*In Ether*).

0·6081 Gm. was dissolved in 250 c.c. of ether and the following results were obtained.

	1st day.	2nd day.	After a month.
P.c. of enol ...	83	89	87

(*In* cyclo*Hexane*).

0·58 Gm. was dissolved in 75 c.c. of *cyclo*hexane; 81% of enol was found in freshly prepared solution.

*Hydroymethylene-o-methyl*cyclo*hexanone*.
Percentage of enol = 46.

The laboratory temperature during these experiments was on an average 27°.

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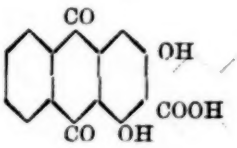
On Munjistin. Part I.

By Prafulla Chandra Mitter and Asoke Kumar Sen.

The main constituents of the colouring matter of madder, both Indian and European, can be divided into two groups: (*a*) hydroxyanthraquinones containing only hydroxyl groups like alizarin, purpurin, purpuroxanthin and (*b*) those containing hydroxy groups along with methyl (or carboxyl) groups like rubiadin, munjistin pseudopurpurin, etc. The constitution of all these compounds is known with the solitary exception of munjistin.

Stenhouse first discovered this compound in the Indian madder, *Rubia munjista* (*Annalen*, 1864, **130**, 325) and suggested that it was purpuroxanthin carboxylic acid. This was confirmed by Schunk and Römer (*Ber.*, 1877, **10**, 172, 790). They showed that it gives phthalic acid on oxidation and when heated gives purpuroxanthin and carbon dioxide. The structure of munjistin is, therefore, either (I) or (II).



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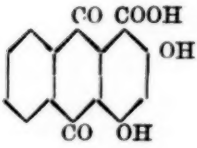
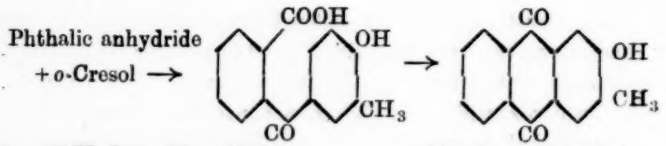


II

A review of the constitutions of naturally occurring anthraquinone derivatives whose structures have been correctly determined reveals the fact that invariably the methyl (or carboxyl) group is in a β-position. Not a single exception to this rule has been hitherto found in nature. So it seemed probable that munjistin contains the carboxyl group in β-position ; or, in other words that it is the oxidation product of rubiadin. We therefore attempted the synthesis of the substance (I) by the oxidation of rubiadin.

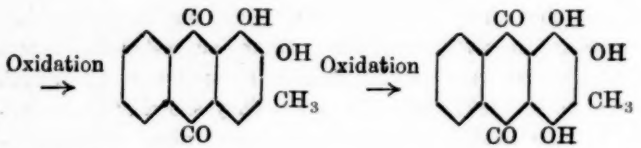
The synthesis of rubiadin as carried out in this laboratory (This *Journal*, 1928, **5**, 25) starting with dioxy-*p*-toluic acid gives an extremely poor yield. Attempts were made to increase the yield by

varying the concentration of fuming sulphuric acid used for sulphonation and the temperature but to no avail. The preparation of dioxy-*p*-toluic acid was then attempted over the dinitro compound, but without success. Recourse was then taken to the following scheme analogous to the synthesis of alizarin, purpurin and purpuroxanthin from β-oxyanthraquinone.



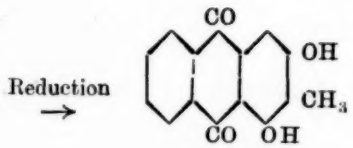
4′-Hydroxy-3′-methyl-2-benzoyl benzoic acid (III)

2-Hydroxy-3-methyl-anthraquinone (IV)



3-Methylalizarin. (V).

3-Methyl-purpurin (VI).



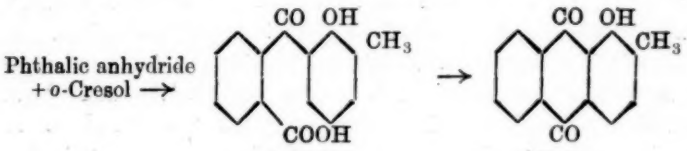
Rubiadin. (VI)

In order to ascertain the best methods of oxidation of hydroxymethylanthraquinones with hydroxyl group contiguous to the methyl group it was also considered desirable to perform some preliminary experiments with easily available hydroxymethylanthraquinones having such structure and we thought of preparing 1-hydroxy-2-methylanthraquinone by condensing *o*-cresol with phthalic anhydride according to the method of Bently, Gardner and Weizmann (*J. Chem. Soc.*, 1907, **91**, 163). They had condensed phthalic anhydride and *o*-cresol in two different ways and got two

different compounds. By condensing the two compounds in boric acid medium they obtained 1-hydroxy-2-methylanthraquinone, m.p. 184°; and by condensing *o*-cresol methyl ether with phthalic anhydride in carbon disulphide using aluminium chloride as the condensing agent they obtained another anthraquinone (m.p. over 300°) and which they considered to be 1-methyl-2-hydroxyanthraquinone (*ibid*).

Attempt was made to obtain 1-hydroxy-2-methylanthraquinone by condensing *o*-cresol and phthalic anhydride with boric acid but the yield was extremely poor.

Ullmann (*Ber.*, 1919, **52**, 2105) had obtained two benzoyl-benzoic acids by condensing *o*-cresol and phthalic anhydride in acetylene tetrachloride medium and this experiment was repeated by us. Two benzoyl-benzoic acids were obtained, one melting at 223° and another at 196°. The latter acid (m. p. 196°) was identical with the one obtained by Weizmann by condensing phthalic anhydride and *o*-cresol in presence of boric acid and it was clearly the result of *ortho* condensation.



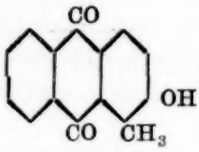
(VII). M.p. 196°

(VIII) 1-Oxy-2-methyl-anthraquinone, m.p. 184°.

The other product melting at 223°—and this was the main product—must therefore be the result of *para*-condensation, and should have the structure (III).

The benzoyl benzoic acid when heated with sulphuric acid at 100° gave an anthraquinone melting at 184° (Formula VIII) identical with that obtained by Weizmann. Curiously enough the benzoyl benzoic acid (Formula III) gave on heating with sulphuric acid at 100° an anthraquinone melting at 211-12°. No such compound has been described in the literature. On methylation however and heating for 20 minutes at 155° in sulphuric acid, the same benzoyl benzoic acid (Formula III) gave a methoxyanthraquinone melting at 184° as well as its demethylation product, an anthraquinone melting at 299° as observed by Weizmann.

It may be noted that the benzoic acid (III) can give rise to two different anthraquinones.

(IV). ← (III) →  (IX).

and these (IV and IX) must represent the formula of the two different anthraquinones, m.p, 211-212° and 299° respectively.

Weizmann had ascribed formula (IX) to his compound melting over 300° on the ground that Froude (*Annalen*, 1882, **202**, 165) had obtained a compound melting at 262° by condensing phthalic anhydride and *o*-cresol with sulphuric acid and had given to it the formula (IV). Bistrzycki and Zen-Ruffinen (*Helv. Chim. Acta*, 1920, **3**, 369) have synthesised the same anthraquinone, m.p. 299° *via* anthrone and from the mode of preparation they say that it must have formula (IV). They had also established the identity of Froude's compound with this by comparison of their acetyl derivatives. To decide which of the two anthraquinones melting at 211-12° and melting at 299° has the structure (IV), the compound melting at 299° was distilled with zinc dust. The product obtained was found to be β-methylanthracene which proves beyond dispute the constitution (IV) for the anthraquinone melting at 299°. The anthraquinone melting at 211-212° is therefore 1-methyl-2-hydroxyanthraquinone. The compound obtained by Froude (*loc. cit.*) which softened at 182° (1-hydroxy-2-methylanthraquinone melts at 184°) and melted at 260-262°, with partial decomposition was evidently a mixture of three anthraquinones, 1-hydroxy-2-methyl-, 1-methyl-2-hydroxy-, and 2-hydroxy-3-methyl-anthraquinone.

The 2-hydroxy-3-methylanthraquinone (IV), gave on alkali fusion, 3-methylalizarin identical with the compound obtained by Froude (*loc. cit.*).

The crude methyl alizarin was oxidised according to the method of D.-R.P. No. 260765. The product obtained could not be crystallised. On sublimation red crystals resembling purpurin were obtained, melting at 234-35°. The compound is identical with the methylpurpurin prepared by Eder and Manoukian by nitrating 1-oxy-3-methylanthraquinone and replacing the nitro group by

hydroxyl group by heating with concentrated hydrochloric acid (*Helv. Chim. Acta*, 1926, **9**, 51). The yield of 3-methylpurpurin was very poor and though attempt was made to reduce it to rubiadin (VI) with alkaline stannous chloride no product could be isolated.

Preliminary experiments on the oxidation of hydroxy methyl anthraquinones were made with 1-methyl-2-oxyanthraquinone. The idea was to see which oxidising agent would work best with the compounds having hydroxyl and methyl groups in adjoining positions, their resistance to oxidation being well known. Chromic acid was first tried but the compound completely broke up even when the reaction was carried out in acetic acid and acetic anhydride media. Some work of Noyes (*Ber.*, 1883, **16**, 52) suggested that such compounds might be oxidised by alkaline ferricyanide. On boiling with potassium hydroxide and potassium ferricyanide, a product was obtained which was distinctly acid but this could not be crystallised by any means whatsoever.

The case with which alizarin passed to purpurin suggested that natural munjistin may be oxidised to purpurin carboxylic acid thereby throwing light on its constitution. Extraction of natural munjistin is a very laborious and lengthy process and only 0·4 gms. was obtained by working up 10 lbs. of powdered root of *R. Munjista*. When 0·3 gm. was subjected to oxidation a red mass was obtained in such a small quantity that it could not be purified.

The experiments are being continued.

Experimental.

Preparation of 2'-Hydroxy-3'-methyl-2-benzoylbenzoic acid (VII) *and 4'-Hydroxy-3'-methyl-2-benzoylbenzoic acid* (III).

o-Cresol (50 g.) was condensed with phthalic acid (50 g.) with the help of aluminium chloride according to the method of Ullmann, (*Ber.*, 1919, **52**, 2105). Yield 54 gms. of crude acid. It was crystallised from glacial acetic acid when 34 gms. of benzoyl benzoic acid (III) melting at 223° were obtained. The mother-liquor when heated and diluted with hot water yielded 5 gms. of a crystalline acid (VII) melting at 196°.

1-Methyl-2-hydroxyanthraquinone (IX).

The benzoyl benzoic acid (III) was dissolved in sulphuric acid (sp. gr. 1·84) and heated on the water-bath for 30 minutes. It was then poured into water. A greenish mass was obtained which when crystallised from glacial acetic acid melted at 211-12° (yield, 5 gms.). (Found: C, 75·77 ; H, 4·1. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2 per cent.)

Acetylation of 1-*Methyl-2-hydroxyanthraquinone.*

The obove anthraquinone (5 g.) was boiled with acetic anhydride and a drop of pyridine for 4 hours. On cooling, the acetyl compound (4·5 gms.) crystallised out; m.p. 125°. (Found: C, 72·48 ; H, 4·4. $C_{17}H_{12}O_4$ requires C, 72·8 ; H, 4·3 per cent.)

Oxidation of 1-*Methyl-2-hydroxyanthraquinone.*

The anthraquinone (4 gms.) was boiled for 4 hours with potassium ferricyanide (50 g.) and caustic potash (23 g. in 200 c.c. of water) under reflux. The solution was filtered and on acidifying with hydrochloric acid a dirty yellow precipitate was obtained. It was filtered and dissolved in sodium carbonate solution. On acidifying a yellow precipitate was obtained. It was then digested with calcium carbonate, filtered and acidified. The yellow precipitate (about 1 gm.) could not be crystallised or sublimed.

4′-Methoxy-3′-methyl-2-benzoyl-benzoic acid.

The compound (25 g.) was obtained in the usual way by dissolving the acid (III) in potassium hydroxide and adding dimethyl sulphate gradually with shaking. Yield 15 gms.. It melted at 176°.

2-Hydroxy-3-methylanthraquinone (IV).

4′-Methoxy-3′-methyl-2-benzoyl benzoic acid (25 g.) was dissolved in pure sulphuric acid (sp. gr. 1·84) and heated at 155° for 30 minutes. It was then poured into ice when a dirty green mass was obtained. This was dissolved in dilute boiling potassium hydroxide solution. It was filtered and on acidifying the filtrate a greenish precipitate was obtained which crystallised from a large volume of glacial acetic acid; m. p. 299° (yield, 8 gms.).

2-Methoxy-3-methylanthraquinone.

The residue left in the above preparation after dissolving the mass in potassium hydroxide solution was crystallised from glacial acetic acid; m.p. 184° (yield, 1 gm.).

Acetylation of 2-Hydroxy-3-methylanthraquinone.

The acetyl compound was prepared in the usual way by boiling with acetic anhydride and a drop of pyridine for 3 hours. The product crystallised from acetic anhydride and gave almost theoretical yield; m.p. 176°.

Distillation with Zinc Dust.

The hydroxy-methylanthraquinone (IV) (2 gm.) was mixed with zinc dust (100 g.) and carefully heated in a current of hydrogen. After two hours the sublimate at the front end was scraped out and boiled with sodium hydroxide but nothing went into solution. It was filtered and crystallised twice from acetic acid when beautiful yellowish flakes were obtained melting at 201°. This appeared to be identical with β-methylanthracene, m.p. 203°.

3-Methylalizarin (V).

2-Hydroxy-3-methyl-anthraquinone (2 g.) was dissolved in potassium hydroxide solution (20 c.c. of 50%) and heated in a nickel crucible in an oil-bath at 200-205° for 3 to 4 hours. The reaction was complete when a small portion dissolved in potash solution with violet colour. The melt was poured in 400 c.c. of water and boiled for 30 minutes. On acidifying, a flocculent black precipitate came down. This was filtered and repeatedly treated with barium hydroxide solution till the filtrate was practically colourless. The residue was suspended in water and decomposed with hydrochloric acid. It was filtered and the residue was dried and extracted repeatedly with benzene. On evaporating off the benzene, 0·5 gm. of a yellowish mass was obtained which could not be crystallised. A portion was sublimed when beautiful yellow crystals, m.p. 245-46°, were obtained. (Found: C, 70·5 ; H, 3·8. $C_{15}H_{10}O_4$ requires C, 70·86; H, 3·9 per cent.).

Acetyl derivative.—It was prepared in the usual way, m.p. 262°. The amount prepared was not sufficient for an analysis.

3-*Methyl-purpurin.*

Crude 3-methylalizarin (0·5 g.) was dissolved in 10 c.c. of sulphuric acid (sp. gr. 1·84), cooled below 15° and while stirred mechanically, 0·5 gm. of manganese dioxide was added gradually in small quantities. The reaction was complete when a small portion of reaction mixture gave a red colour with alkali. The whole mixture was poured into a litre of water and acidified with sulphurous acid when a flocculent red precipitate came down. This on purification by sublimation—it could not be crystallised from any solvent—melted at 234°. Yield 0·1 gm. (Found: C, 66·3; H, 3·7. $C_{15}H_{10}O_5$ requires C, 66·6; H, 3·7 per cent.).

Acetyl derivative.—This was prepared in the usual way and melted at 287°.

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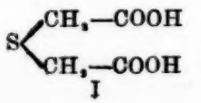
A Theory of Colour on the Basis of Molecular Strain. Part VI.—Effect of Sulphur on Colour.

By Amarendra Nath Dey and Sikhibhusan Dutt.

In a series of papers from this laboratory (Tewari and Dutt, this *Journal*, 1926, **3**, 161 ; 1927, **4**, 201 ; 1928, **5**, 59) the effect of nitrogen on colour has been studied at length, and in that connection it was thought that it would be interesting to find out what effect an atom of sulphur has on the colour of organic dyestuffs.

It is well-known that thiopyronine in which an atom of sulphur has replaced the pyrone oxygen atom of Pyronine G is much deeper in colour than the latter. Similarly Purvis, Jones and Tasker, (*J. Chem. Soc.*, 1910, **97**, 2287) have shown that the thio-oxal ates are deeper in colour than the corresponding oxalates which are by themselves colourless. Dutt and Watson (*J. Chem. Soc.*, 1922, **121**, 1939, 2414) also have shown that many mercaptan derivatives of azo-dyes and thio-fluorescein are deeper in colour than the corresponding dyes containing oxygen in place of sulphur. This conclusion is borne out by the recent researches of Reid and his collaborators (Reid, *J. Amer. Chem. Soc.*, 1924, **46**, 1936, 1926 ; 1926, **48**, 19, 528).

In all the above cases where sulphur replaces an oxygen atom it produces an increase of colour probably because of the fact that though, like oxygen, it is divalent and potentially quadrivalent it has got much greater atomic weight and necessarily its loading effect is more intense. Therefore it will be expected that when a sulphur atom replaces a carbon atom a similar intensification of colour will take place. An interesting case for verification of such an expectation would be to prepare a series of pyronine dyestuffs from thiodiglycollic acid (I).



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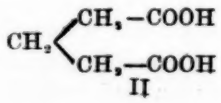

II

and compare them with the corresponding dyestuffs derived from glutaric acid (II), a number of which has already been described by Dutt and Thorpe (*J. Chem. Soc.*, 1924, **125**, 2524 ; Dutt, *ibid*, 1926, **129**, 1132).

The dyestuffs described in this paper have a deeper colour than the corresponding dyes of the glutaric acid series. Further quantitative work regarding this is being done in this laboratory.

Experimental.

Thiodiglycollic Acid.—Chloracetic acid (95 g.) was added little by little to a solution of sodium carbonate (145 g.) dissolved in the minimum quantity of water. Caustic soda (45 g.) was next dissolved in about a 100 c.c. water and the solution was divided in two parts, one of which was saturated with sulphuretted hydrogen gas and the two halves were simultaneously added with constant stirring to the solution of sodium chloracetate. The whole mass becomes pasty. It is left as such for about two to three hours. Next concentrated sulphuric acid (100 gm.) is added carefully and the hot solution is filtered and left overnight, crude thiodiglycollic acid separates which is filtered off and recrystallised from water, m. p. 129°.

Resorcinolthiodiglycollein.—Thiodiglycollic acid (3 g.) was mixed with resorcin (4·4 g.) and the mixture was heated to a temperature of about 150° and kept at that temperature. A few drops of sulphuric acid were used as a condensing agent. When the viscous mass became solid it was powdered and treated with hot water. Then it was dissolved in caustic soda and filtered and the dye precipitated by dilute hydrochloric acid. It was filtered and washed thoroughly and redissolved in caustic soda and precipitated again by dilute acetic acid. It does not melt up to 310° and dissolves in alcohol. In alkaline solutions it shows a yellow colour with a green fluorescence. (Found : S, 9·46. $C_{16}H_{12}O_5S$ requires S, 16·01 per cent.).

Phloroglucinolthiodiglycollein.—Thiodiglycollic acid (3 g.) and phloroglucinol (4·4 g.) were heated together at 170°-180° for 6 hours, few drops of sulphuric acid being added as a condensing agent. The solid mass was thoroughly powdered and extracted by means of caustic soda solution and filtered. The dye was precipitated by

dilute hydrochloric acid. It dissolves in many of the organic solvents. In caustic alkali it shows an orange colour. It could not be crystallised. (Found: S, 9·0. $C_{16}H_{12}O_7S$ requires S, 9·2 per cent.).

Phenolthiodiglycollein.—Thiodiglycollic acid (5 g.) was mixed with phenol (4·2 g.) and tin tetrachloride (5 g.) and heated for about 8 hours at 110°-120°. The viscous melt was next treated with dilute ammonia and filtered. The filtrate was treated with hydrochloric acid. The precipitated dye was collected could not be crystallised from alcohol, acetic acid, and chloroform. Brown powder dissolving in alkalis with deep red colour, m. p. 129°. (Found: S, 11·02. $C_{16}H_{14}O_4S$ requires S, 10·6 per cent.).

4 : 4-*Tetraethyldiamino*-2 : 2-*amidophenylthiodiglycollein.*—Thiodiglycollic acid (3 g.) and *m*-diethylamidophenol (3 g.) were heated with a few drops of sulphuric acid for about 6 hours at 130°-140°. The tarry mass was next dissolved in hydrochloric acid and filtered. The dye was precipitated by a cold dilute solution of sodium carbonate. The dye was obtained as a dull pink amorphous powder which could not be crystallised, m. p. 172°-173°. (Found: S, 7·2. $C_{24}H_{30}O_3N_2S$ requires S, 7·5 per cent.).

4 : 4-*Diamino*-2 : 2-*iminophenylthiodiglycollein.*—Thiodiglycollic acid (3·3 g.) was heated with *m*-phenylenediamine hydrochloride (6 g.) to a temperature of about 220° and kept at that temperature for about an hour. The hard mass on cooling was powdered and refluxed with absolute alcohol. It was filtered and the filtrate reduced to a small bulk and filtered again from the solid residue that was deposited. The filtrate was then treated with water. The dye separates as pale yellow powder, dissolving in alcohol with an yellow colour having green fluorescence. It melts at 241°. (Found: S, 9·9. $C_{16}H_{15}N_3O_2S$ requires S, 10·2 per cent.).

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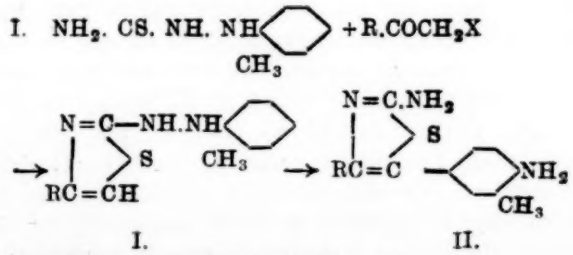
Benzidine Rearrangement in Heterocyclic Series. Part II.

By Prafulla Kumar Bose and Bijon Kumar Sen.

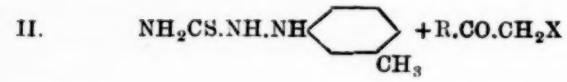
It is well known that aromatic hydrazo compounds undergo benzidine transformation under the influence of mineral acids. In this isomeric change two aromatic nuclei are involved. The question naturally arises: Do hydrazo compounds containing one or two heterocyclic nuclei behave similarly when subjected to similar treatment? So far as the present authors are aware no systematic investigation has yet been made to settle this question. A couple of instances are however known which are very interesting from the point of view of the present investigation. Fargher and Pyman (*J. Chem. Soc.*, 1919, **115**, 222; *cf.* also Pyman and Ravald, *ibid*, 1920, **117**, 1426) found that a rearrangement of the benzidine type could occur in a compound of the hydrazobenzene type containing a glyoxaline ring in place of a benzene ring. Further one of us (Bose, *J. Indian Chem. Soc.*, 1927, **4**, 331) has recently shown that a similar change also takes place when one of the nuclei happens to be a thiazole.

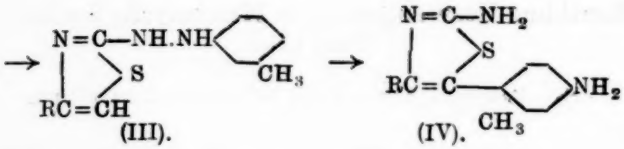
The present investigation was undertaken with a view to study some more cases of benzidine and semidine rearrangement in heterocyclic series. It was expected that the condensation of 1-*o*-tolylthiosemicarbazide or 1-*m*-tolylthiosemicarbazide with halogenated ketones will give rise to hydrazo compounds which will undergo benzidine rearrangement, thus:



I. II.

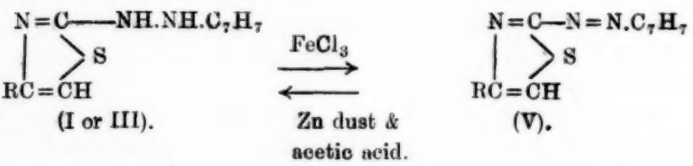
(X = Halogen; R = Alkyl or ayrl group)

II. 



This expectation has fully been realised.

The condensation takes place smoothly at the room temperature between equimolecular quantities of the reactants in alcoholic medium. The hydrazo-compounds (I or III) thus obtained give characteristic colour reactions with concentrated sulphuric acid, and are found to be affected by light and air. They give rise to mono-acetyl derivatives with great ease and are oxidised by ferric chloride to the corresponding azo compounds (V). The azo compounds give colour reactions characteristic of the respective hydrazo-compounds and are reconverted into the original hydrazo compounds by the action of zinc dust and acetic acid. Thus:

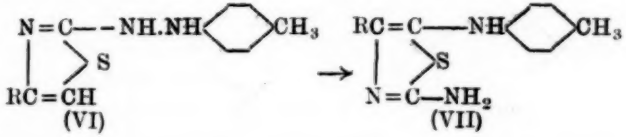


The hydrazo-compounds (I or III) are easily transformed into the isomeric bases (II or IV), when boiled with dilute hydrochloric acid for a few minutes.

The results of this investigation when considered along with those recorded by Pyman and his collaborators and by Bose lend support to the view put forward by Fargher and Pyman in the case of the glyoxaline derivatives, namely that the condition which essentially determines the isomeric change is the linking between the carbon atoms that are involved in a change of the benzidine type. In other words, a conjugated system of double bonds which connects the 1 and 4 carbon atoms of a benzene nucleus must be present in a heterocyclic ring before the latter can qualify for the isomeric change. In the case of the thiazole ring in formula (I or

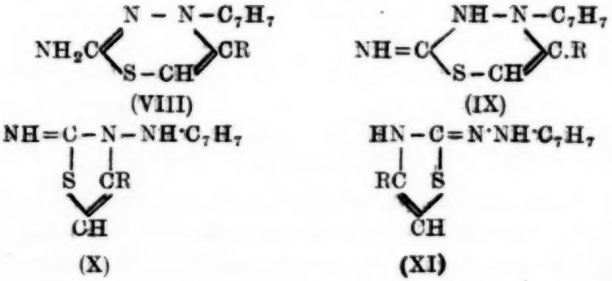
III), it will be seen that the 2- and 5-carbon atoms are connected by alternate single and double bonds and as such they behave like hydrazo-benzene.

The next attempt was to condense 1-*p*-tolyl-thiosemicarbazide with halogenated ketones. In this case it was expected that if the condensation occurred normally, the products having a *para*-substituted nucleus would suffer semidine change under the influence of mineral acids (*cf.* Michaelis and Schäfer, *Annalen*, 1915, **407**, 229) thus:



(VI) (VII)

The condensation of 1-*p*-tolyl-thiosemicarbazide with halogenated ketones proceeded smoothly at the room temperature. The products, however, on boiling with dilute hydrochloric acid, split off ammonia and were converted into keto-compounds. To understand the nature of such a change it is necessary at this stage to indicate the various possibilities, which an 1-substituted-thiosemicarbazide (having various reactive centres) presents during condensation with a halogenated ketone. In fact one can expect besides (VI) as many as four different products * of condensation, namely—



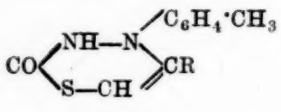
(VIII) (IX)

(X) (XI)

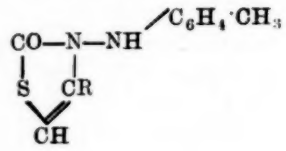
* For the formulation of these compounds the halogen of the ketone has been supposed to be eliminated with the "thiol" hydrogen of the thiosemicarbazide. This is followed by ring closure. That the "thio" part is more reactive towards halogenated ketones than the imino or amino groups has been supported by the researches of Dixon and Taylor (*J. Chem. Soc.*, 1912, **101**, 2502), of Walther and Roch (*J. pr. Chem.* 1913, (ii), **87**, 27), of Bose (*J. Indian Chem. Soc.*, 1924, **1**, 51), and others.

Of these only (IX) and (X) can give rise to keto compounds with simultaneous formation of ammonia by hydrolysing agents. In one case (IX) the resulting product would be an 1:3:4-thiodiazine (XII) and in the other case (X), a thiazole (XIII).

The keto compounds were found to be quite stable and were insoluble in caustic alkalis. This evidence seems to be in favour of the formula (XIII) for the keto compound. Consequently the condensation products should be represented by (X).



(XII)



(XIII)

Experimental.

Preparation of 1-o-*Tolylthiosemicarbazide*.—o-Tolylhydrazine (12·2 gms.), freshly prepared alcoholic hydrochloric acid (prepared by passing 3·65 gms. of dry hydrochloric acid gas through 20 c.c. of absolute alcohol in the cold), and potassium sulphocyanide (14·55 g.) were heated on a water-bath under reflux for nearly 12 hours. The contents of the flask, on cooling, were poured into cold water and a solid mass separated which was collected and washed with water several times. The product was finally crystallised from dilute alcohol in colourless plates, m.p. 163-64°. It is easily soluble in cold acetone, alcohol and pyridine but insoluble in water. Yield, 8 gms. (Found: N, 23·3. $C_8H_{11}N_3S$ requires N, 23·2 per cent.).

2-o-*Tolylhydrazino*-4-*phenyl*-1:3-*thiazole* (*Formula* I, R=C_6H_5).

Finely powdered 1-o-tolyl-thiosemicarbazide (·9 g.) and ω-bromo-acetophenone (1 gm.) were shaken with 10 c.c. of absolute alcohol at the room temperature, without application of heat. The components gradually dissolved with evolution of heat. After about 15 minutes, the hydrobromide of the base crystallised out. Nearly 5 c.c. of pyridine were then added, when the crystals dissolved. On diluting with water white crystals of the free base separated out. These were collected, washed with water and dilute alcohol and dried. The yield of the crude product was 1·5 gms. It was

finally crystallised from dilute alcohol in pale brown needles, m.p. 175°–180° with decomposition. (Found: N, 14·62. $C_{16}H_{15}N_3S$ requires N, 14·95 per cent.).

The subs tance gives a blue colouration with conc. sulphuric acid; the colour vanishes on dilution. It turns brown when kept exposed to air. It is soluble in alcohol, acetone, pyridine but insoluble in water.

Acetyl derivative.—The acetyl derivative was obtained by heating the base with acetic anhydride and a drop of pyridine for a few minutes. It was crystallised twice from dilute alcohol in white star-like aggregates, m.p. 152°. (Found: N, 13·12. $C_{18}H_{17}ON_3S$ requires N, 13·01 per cent.).

2-o-*Tolyl-azo*-4-*phenyl*-1:3-*thiazole* (Formula V, R = Ph).

2-*o*-Tolylhydrazino-4-phenyl-1:3-thiazole (1 gm.) was taken up with 5 c.c. of alcohol and nearly 2 gm. of ferric chloride were added to it. The mixture was heated on a water-bath for nearly two hours under reflux. The contents were cooled and about 2 c.c. of conc. hydrochloric acid were added. On diluting the contents of the flask with cold water, orange coloured crystals separated out. This was re-crystallised from dilute alcohol in beautiful orange plates with a golden lusture, m.p. 110°. It is slightly soluble in water and easily soluble in alcohol, pyridine and acetone. It dyes wool a yellow shade and gives deep blue coloration with concentrated sulphuric acid. It refused acetylation. (Found: N, 15·15. $C_{16}H_{13}N_3S$ requires N, 15·07 per cent.).

It gave, on reduction with zinc dust and dilute acetic acid, the hydrazo compound from which it had been derived.

In this connection it has been found that the hydrazo compounds described by Bose (*loc. cit.*) which are also similarly constituted are oxidised by ferric chloride under the conditions stated above to the corresponding azo-compounds. Thus, 2-pheylhydrazino-4-phenyl-1:3-thiazole is oxidised to 2-*benzene-azo*-4-*phenyl*-1:3-*thiazole* which forms bright orange needles, m.p. 117°. It dyes wool yellow shade. (Found: N, 15·84. $C_{15}H_{11}N_3S$ requires N, 15·85 per cent.).

2-Phenyl-hydrazino-4-*p*-tolyl-1:3-thiazole gave 2-*benzene-azo*-4-p-*tolyl*-1:3-*thiazole*, which forms small prismatic crystals of deep orange colour from dilute alcohol, m.p. 161°. It dyes wool deep orange shade. (Found: N, 15·03. $C_{16}H_{13}N_3S$ requires N, 15·07 per cent.).

2-Phenylhydrazino-4-methyl-1:3 thiazole was similarly oxidised to *2-benzene-azo-4-methyl-1:3-thiazole*. This was obtained from dilute alcohol in small orange crystals, m. p. 120°. It dyes wool yellow shade. (Found: N, 20·67. $C_{10}H_9N_3S$ requires N, 20·7 per cent.).

Action of Hydrochloric Acid on 2-o-*Tolylhydrazino-4-phenyl-1:3-thiazole: Formation of* 2-*Amino-4-phenyl-5-p-amino* (m)-*tolyl-1:3-thiazole* (*Formula* II, R=Ph).

2-o-Tolylhydrazino-4-phenyl-1:3-thiazole (1·5 gm.) was boiled with nearly 100 c.c. of dilute hydrochloric acid (1:4) till the former dissolved completely. The solution was allowed to cool, filtered and made alkaline with ammonia. A white mass separated out. This was collected, washed with water and crystallised with the aid of animal charcoal as decoloriser from dilute alcohol in pale yellow needles, m. p. 165°. It did not respond to the colour reaction characteristic of its isomeride. It is readily soluble in pyridine, acetone, alcohol and insoluble in water. (Found: N, 15·21. $C_{16}H_{15}N_3S$ requires N, 14·93 per cent.).

The *hydrochloride* crystallised from dilute hydrochloric acid in white needles, m. p. 197°. It was dried in air and finally over sulphuric acid in a desiccator. It is easily soluble in water and alcohol but moderately in acetone. (Found: Cl, 19·19. $C_{16}H_{17}N_3SCl_2$, H_2O requires Cl, 19·1 per cent.).

The *picrate* was prepared by adding to the saturated solution of the base in alcohol, a saturated solution of picric acid in dilute alcohol. It was crystallised finally from dilute acetone in reddish yellow rectangular plates, m. p. 227° with decomposition. (Found: N, 16·53. $C_{22}H_{16}O_6N_6S$ requires N, 17·07 per cent.).

Diacetyl derivative.—On adding acetic anhydride to 2-amino-4-phenyl-5*p*-amino-(*m*)-tolyl-1:3-thiazole, the latter dissolved with evolution of heat. The solution was boiled for sometime and then on pouring the solution into cold water, a crystalline product separated out. It was recrystallised from dilute alcohol, by the aid of animal charcoal as decoloriser, in white rectangular crystals, m. p. 182°. (Found: N, 11·41. $C_{20}H_{19}O_2N_3S$ requires N, 11·51 per cent.).

The *chloroplatinate* was prepared by adding platinic chloride to an alcoholic solution of the base. The product was purified by washing with water and dilute alcohol. It formed dull yellow microscopic crystals, which did not melt below 300°. (Found: Pt, 27·17. $C_{16}H_{15}N_3S$, H_2PtCl_6 requires Pt, 27·51 per cent.).

2-o-*Tolylhydrazino*-4-p-*tolyl*-1:3-*thiazole* (*Formula* I, R=*p*-Tolyl).

From 0·9 gm. of *o*-tolylthiosemicarbazide and 1 gm. of *p*-methyl-*w*-bromacetophenone, 1·6 gm. of the crude product were obtained. The method of preparation was identical with that described under the corresponding phenyl compound (p. 646). It was crystallised from a mixture of pyridine and dilute alcohol in pale brown shining plates, which melt with decomposition at 179°. (Found: N, 14·6. $C_{17}H_{17}N_3S$ requires N, 14·23 per cent.).

It is easily soluble in acetone, alcohol, and pyridine and insoluble in water. It gives a green colour with concentrated sulphuric acid, which vanishes on dilution.

The *acetyl* derivative was crystallised from dilute acetone in fine white needles, m. p. 160°-161°. (Found: N, 12·45. $C_{19}H_{19}ON_3S$ requires N, 12·47 per cent.).

2-o-*Tolyl-azo*-4-p-*tolyl*-1:3-*thiazole* (*Formula* V, R=*p*-Tolyl).

Obtained by oxidising the hydrazo compound with alcoholic ferric chloride solution it formed brick-red crystals(from dilute alcohol), m. p. 148°. It could be reduced to the original hydrazo compound with zinc dust and acetic acid. (Found: N, 14·62. $C_{17}H_{15}N_3S$ requires N, 14·32 per cent.).

It gives a green coloration with concentrated sulphuric acid.

Action of Hydrochloric acid on 2-o-*Tolyl-hydrazino*-4-*p-tolyl*-1:3-*thiazole*: *Formation of* 2-*Amino*-4-p-*tolyl*-5-p-*amino*-(*m*)-*tolyl*-1:3-*thiazole* (*Formula* II, R=*p*-Tolyl).

The base (1 gm.) gave, on being boiled with 100 c.c. of 2·5N hydrochloric acid, 0·6 gm. of the diamine. It crystallised from a mixture of dilute alcohol and pyridine in pale brown needles, m.p. 181°. It is readily soluble in alcohol, acetone, and pyridine and insoluble in water. (Found: N, 14·52. $C_{17}H_{17}N_3S$ requires N, 14·23 per cent.).

The *diacetyl* derivative crystallised from dilute alcohol (animal charcoal used as decoloriser) in white rectangular crystals, m.p. 208°. It is soluble in alcohol, acetone and pyridine but insoluble in water. (Found: N, 10·94. $C_{21}H_{21}O_2N_3S$ requires N, 11·09 per cent.).

The *hydrochloride* of the base crystallised from hydrochloric acid in small shining crystals, m.p. 278° with decomposition. It

was dried first by exposing it to the air and then in a desiccator over sulphuric acid. (Found: Cl, 19·28. $C_{17}H_{19}N_3SCl_2$ requires Cl, 19·28 per cent.).

The *chloroplatinate* of the base was obtained in dull brown microscopic crystals which did not melt below 300° by adding an aqueous solution of platinic chloride to a saturated solution of the base in alcohol. It was purified by washing with water and dilute alcohol. (Found: Pt, 27·7. $C_{17}H_{17}N_3S,H_2PtCl_6$ requires Pt, 27·67 per cent.).

It is slightly soluble in alcohol, acetone and pyridine but insoluble in water.

The *picrate* formed yellow crystals, m.p. 201° (decomp.). (Found: N, 16·26. $C_{23}H_{18}O_6N_6S$ requires N, 16·6 per cent.)

2-o-*Tolylhydrazino*-4-*methyl*-1 : 3-*thiazole* (*Formula* I, R=CH_3).

The product (1·5 gm.) from 1-*o*-tolylthiosemicarbazide (1·8 g.) and chloracetone (1 gm. in 15 c c. alcohol) crystallised from a mixture of pyridine and dilute alcohol in reddish needles which melted and decomposed at 162°. It is insoluble in water but readily soluble in alcohol, acetone and pyridine. It turned red on exposure to air and light. The substance imparts a pink colour to concentrated sulphuric acid; the colour vanishes on dilution. (Found: N, 19·3. $C_{11}H_{13}N_3S$ requires N, 19·2 per cent.).

The *acetyl* derivative was crystallised from dilute acetone, using animal charcoal as a decoloriser, in beautiful white rectangular plates, m.p. 96°. (Found: N, 16·44. $C_{13}H_{15}ON_3S$ requires N, 16·11 per cent.).

Action of Hydrochloric Acid on 2-o-*Tolylhydrazino*-4-*methyl*-1 : 3-*thiazole*: *Formation of* 2-*Amino*-4-*methyl*-5-p-*amino*-(m)-*tolyl*-1 : 3-*thiazole* (Formula II, R=CH_3).

It was first crystallised from a mixture of pyridine and dilute alcohol (animal charcoal used), and then from dilute acetone in pale brown needles, which turned brown on coming in contact with air and light, melting at 144°. It is easily soluble in acetone, alcohol, pyridine but insoluble in water and benzene. It did not respond to the colour reaction characteristic of its isomer. (Found: N, 19·59. $C_{11}H_{13}N_3S$ requires N, 19·17 per cent.).

The *hydrochloride* crystallised from concentrated hydrochloric acid in colourless stout needles, m.p. 261° with decomposition.

The *diacetyl* derivative crystallised from dilute acetone in long prismatic needles, m.p. 266°. (Found: N, 14·26. $C_{15}H_{17}N_3SO_2$ requires N, 13·87 per cent.).

The *picrate* formed yellow crystals (from dilute acetone) with a golden lustre. It begins to decompose at 200° and melts at 247° with complete decomposition. (Found: N, 19·36. $C_{17}H_{13}O_6N_6S$ requires N, 19·6 per cent.).

The *chloroplatinate* of the base formed dull grey microscopic crystals which did not melt below 300°. (Found: Pt, 30·24. $C_{11}H_{13}N_3S$, H_2PtCl_6 requires Pt, 30·97 per cent.).

Preparation of 1-m-*Tolylthiosemicarbazide*.

The preparation of this compound is very similar to that of the *ortho*-compound. The product crystallised in white plates, m. p. 134-35°. It is soluble in alcohol, acetone and pyridine (yield, 9 gms. from 12·2 gms. of *m*-tolylhydrazine). (Found: N, 23·12. $C_8H_{11}N_3S$ requires N, 23·2 per cent.)

2-m-*Tolylhydrazino*-4-*phenyl*-1: 3-*thiazole* (*Formula* III, R=Ph).

ω-Bromo-acetophenone (2 g.) and 1-*m*-tolylthiosemicarbazide (1·8 g.) and 15 c.c. of absolute alcohol were taken. The procedure is similar to that described under 2-*o*-tolylhydrazino-4-phenyl-1:3-thiazole. The product was purified by crystallisation from dilute pyridine. It formed white needle-shaped crystals, m. p. 188° with decomposition. It is soluble in alcohol, acetone, acetic acid, pyridine.

It gives a blue coloration with concentrated sulphuric acid (yield, 3 gm.). (Found: N, 14·03. $C_{16}H_{13}N_3S$ requires N, 14·95 per cent.).

The *acetyl* derivative crystallised from dilute alcohol in white needles, m. p. 145°. It is soluble in acetone, acetic acid, alcohol and pyridine. (Found: N, 13·06. $C_{18}H_{17}N_3SO$ requires N, 13·01 per cent.).

Action of Hydrochloric Acid on 2-m-*Tolyl-hydrazino*-4-*phenyl*-1: 3-*thiazole*: *Formation of* 2-*Amino*-4-*phenyl*-5-p-*amino*-(o)-*tolyl*-1: 3-*thiazole* (*Formula* IV, R=Ph).

The product was crystallised from dilute acetone in pale brown needles, m. p. 135°. It is soluble in acetone, acetic acid, alcohol, pyridine and insoluble in water. It does not give any colour re-

action with concentrated sulphuric acid. Yield, quantitative. (Found: N, 14·85. $C_{16}H_{15}N_3S$ requires N, 14·95 per cent.)

The *hydrochloride* crystallised from dilute hydrochloric acid in white crystals, m. p. 265°-270° with decomposition. (Found: Cl, 19·45. $C_{16}H_{17}N_3Cl_2S$, H_2O requires Cl, 19·1 per cent.)

2-*Acetylamino*-4-*phenyl*-5-p-*acetylamino*-(o)-*tolyl*-1 : 3-*thiazole* was prepared as usual. From dilute acetone, using animal charcoal as decoloriser, it was obtained as white stout crystals, m. p. 235°. (Found: S, 8·85. $C_{18}H_{16}O_2N_3S$ requires S, 8·77 per cent.)

The *picrate* was crystallised from dilute acetone in yellow prismatic crystals, m. p. 215° with decomposition.

2-m-*Tolylhydrazino*-4-p-*tolyl*-1 : 3-*thiazole* (*Formula* III, R=p-Tolyl).

The procedure was identical with that described for 2-*m*-tolylhydrazino-4-phenyl-1 : 3-thiazole. 1·8 Gms. of 1-*m*-tolylthiosemicarbazide, 2·13 gms. of *p*-methyl-*w*-bromo-acetophenone and 15 c.c. of absolute alcohol were taken. The free base (3 gms.) crystallised from dilute pyridine in pale brown needles, m. p. 191° with decomposition. It is soluble in acetone, acetic acid, alcohol and pyridine but insoluble in water. It gives a green colour with concentrated sulphuric acid. It turns brown on exposure to air and light. (Found: S, 10·97. $C_{17}H_{17}N_3S$ requires S, 10·85 per cent.).

The *acetyl derivative* crystallised from dilute acetone in white crystals, m. p. 121°. (Found: N, 12·69. $C_{19}H_{19}N_3SO$ requires N, 12·47 per cent.)

Action of Hydrochloric Acid on 2-m-*Tolyl-hydrazino*-4-p-*tolyl*-1 : 3-*thiazole* : *Formation of* 2-*Amino*-4-p-*tolyl*-5-p-*amino*-(o)-*tolyl*-1 : 3-*thiazole* (Formula IV, R=p-Tolyl).

The diamine formed pale brown needles, m. p. 175°.

It is soluble in alcohol, pyridine, acetone and acetic acid and insoluble in water. It does not give colour reaction with concentrated sulphuric acid. (Found: N, 14·39. $C_{17}H_{17}N_3S$ requires N, 14·23 per cent.)

The *acetyl* derivative crystallised from dilute acetone, using animal charcoal as decoloriser, in stout needles, m. p. 248°. (Found: N, 11·12. $C_{21}H_{21}N_3SO_2$ requires N, 11·09 per cent.)

The *hydrochloride* crystallised from dilute hydrochloric acid in stout white crystals, m. p. 247°. (Found: Cl, 19·45. $C_{17}H_{19}N_3SCl_2$ requires Cl, 19·28 per cent.)

The *picrate* formed yellow needles, m. p. 202° (from dilute alcohol).

2-m-*Tolylhydrazino*-4-*methyl*-1:3-*thiazole* (Formula III, R=CH_3)

The method of preparation is similar to that adopted for 2-*o*-tolyl hydrazino-4-methyl-1: 3-thiazole. 1·8 Gms. of 1-*m*-tolyl thiosemicarbazide and 1 gm. of monochloro-acetone and 15 c.c. of alcohol were taken. The product formed reddish needles from dilute pyridine, m.p. 135°, with decomposition. It is soluble in acetone, alcohol, pyridine, acetic acid and insoluble in water. It readily turns brownish red on exposure to air and light. Yield, 1·2 gms. It imparts a pink colour to conc. sulphuric acid, the colour vanishes on dilution with water. (Found: N, 18·86. $C_{11}H_{13}N_3S$ requires N, 19·2 per cent.)

Acetyl derivative.—It crystallised from dilute acetone, using animal charcoal as decoloriser, in colourless prismatic crystals, m.p. 119°. (Found: N, 16·09. $C_{13}H_{16}OSN_3$ requires N, 16·11 per cent.).

Action of Hydrochloric Acid on 2-m-*Tolylhydrazino*-4-*methyl*-1:3-*thiazole*: *Formation of* 2-*Amino*-4-*methyl*-5-p-*amino*-(o)-*tolyl*-1:3-*thiazole* (Formula IV, R=CH_3).

The diamine formed yellow needles, m.p. 157°. It is soluble in acetone, alcohol, pyridine, acetic acid and insoluble in water. It gives no colour reaction with conc. sulphuric acid. Yield 60 per cent. (Found: N, 19·36. $C_{11}H_{13}N_3S$ requires N, 19·19 per cent.).

The *acetyl* derivative crystallised from dilute acetone in white plates, m.p. 236°. (Found: N, 13·9. $C_{15}H_{17}N_3SO_2$ requires N, 13·87 per cent.).

The *hydrochloride* crystallised from dilute hydrochloric acid in fine white feathery needles, m.p. 263°, with decomposition.

The *picrate* crystallised from dilute alcohol in yellow crystals, m.p. 212°, with decomposition.

Preparation of 1-p-*Tolylthiosemicarbazide.*—Following the usual procedure, about 4·5 gms. of the product were obtained from 10 gms. of *p*-tolylhydrazine hydrochloride (in 40 c.c. of alcohol).

It was crystallised from dilute alcohol in colourless hexagonal plates, m.p. 174°. The reported m.p. of this compound prepared by Pellizzari and Ferro (*Gazzetta*, 1898, **28**, *ii*, 560) is 150°. (Found: S, 17·6. $C_8H_{11}N_3S$ requires S, 17·68 per cent.)

It is easily soluble in acetone, pyridine or aqueous alkali but not in benzene. Attempts to improve the yield by carrying on the reaction in sealed tubes or by substituting ammonium sulphocyanide for the potassium salt were fruitless.

1-p-*Tolylthiosemicarbazide and w-Bromo-acetophenone: Formation of* 2-*Imino*-3-p-*toluidino*-4-*phenyl*-2:3-dihidro-1:3-*thiazole* (Formula X, R=Ph).

The condensation was carried out and the product isolated as in the case of 1-*o*-tolylthiosemicarbazide and *w*-bromo-acetophenone. The base crystallised from acetone in colourless needles, m.p. 193°, with decomposition. It is also soluble in pyridine, but only sparingly in alcohol. It gave a deep blue coloration with concentrated sulphuric acid. (Found: N, 14·98. $C_{16}H_{16}N_3S$ requires N, 14·95 per cent.).

Acetyl derivative.—It formed long colourless needles (from alcohol); m.p. 147°. (Found: C, 66·63. H, 5·34. $C_{18}H_{17}N_3SO$ requires C, 66·88, H, 5·26 per cent.).

2-*Keto*-3-p-*toluidino*-4-*phenyl*-2:3-*dihydro*-1:3-*thiazole*. (Formula XIII, R=Ph.)

The imino compound described above (1·5 gm.) was boiled with 1·5 N-hydrochloric acid (100 c.c.) for about half an hour and filtered hot from a small amount of orange insoluble matter. The filtrate was cooled and just made alkaline with caustic soda, when the solution turned milky and the smell of ammonia was noticeable. A pale yellow precipitate began to settle down very slowly. This was collected after a couple of hours, washed with cold water and dried (1·2 gm.). It freely dissolved in methyl or ethyl alcohol, acetone and dilute acids.

The substance was purified by crystallisation from benzene by the addition of ligroin. It formed transparent yellow plates, m.p. 210°-211°. It is insoluble in alkali. (Found: C, 67·59; H, 5·13; N, 10·18. $C_{16}H_{14}ON_2S$ requires C, 68·08; H, 4·96; N, 9·93 per cent.).

2-*Imino*-3-p-*toluidino*-4-*methyl*-2:3-*dihydro*-1:3-*thiazole*.
(Formula X, R=CH_3).

The procedure for the condensation of 1-*o*-tolyl-thiosemicarbazide and monochloroacetone was followed in this case. The base crystallised from a mixture of pyridine and alcohol in reddish needles, m.p. 168-69°. (Found: C, 59·94; H, 6·02. $C_{11}H_{13}N_3S$ requires C, 60·28; H, 5·94 per cent.).

The p-*tolyl-thiocarbimide derivative* crystallised from dilute acetone in pale brown needles, m.p. 143°. (Found: N, 15·22. $C_{19}H_{20}N_4S_2$ requires N, 15·22 per cent.).

2-*Keto*-3-p-*toluidino*-4-*methyl*-2:3-*dihydro*-1:3-*thiazole*.
(Formula XIII, R=CH_3).

The imino compound (0·7 gm.) was boiled with N-hydrochloric acid (25 c.c.) for about an hour. The brown precipitate obtained by neutralising the acid, crystallised from dilute methyl alcohol (animal charcoal used) in hard, pale yellow crystals, m.p. 177°. (Found: N, 12·87. $C_{11}H_{12}ON_2S$ requires N, 12·73 per cent.).

2-*Imino*-3-p-*toluidino*-4-p-*tolyl*-2:3-*dihydro*-1:3-*thiazole*.
(Formula X, R=*p*-Tolyl.)

The condensation was carried out as in the case of 1-*o*-tolyl-thiosemicarbazide and *p*-methyl-*w*-bromo-acetophenone, the yield being quantitative. The base crystallised from alcohol and pyridine in pale brown needles, m.p. 184°, with decomposition. (Found: N, 14·25. $C_{17}H_{17}N_3S$ requires N, 14·24 per cent.).

The *acetyl derivative* formed glistening needles (from alcohol), m.p. 155°. (Found: N, 12·72. $C_{19}H_{19}ON_3S$ requires N, 12·46 per cent.).

The p-*tolyl-thiocarbimide derivative* crystallised from dilute acetone in pale yellow, shining plates, m.p. 152°.

Our thanks are due to Sir P. C. Rây for his kind interest during the investigation.

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and Technology, Calcutta.

Received August 30, 1928

A New Gravimetric Method for the Estimation of Lead.

I. Purely from its soluble salts.

By P. N. Das-Gupta, G. C. Roy and K. M. Sil.

When a solution of lead nitrate is treated with alkaline hydrogen peroxide, an orange colored precipitate of the empirical composition Pb_5O_7, $3H_2O$ is obtained. This was first noticed by Brauner (*Zeit. anorg. Chem.*, 1894, **7**, 2) who considered it as a definite compound.

We have however observed that except when the alkalis, sodium or potassium hydroxide used, are very weak, the precipitation is never complete ; on the other hand, if sodium or potassium hydroxide solution be replaced by ammonium hydroxide, the precipitation of lead becomes quantitative. This observation serves as the basis of a quantitative estimation of lead from solution of its salts, which forms the subject matter of the present paper.

The influence of the presence of salts such as potassium nitrate, ammonium acetate, sodium acetate, and ammonium nitrate on the precipitation has been studied and the colour of the precipitates in each case has been found to vary somewhat gradually from orange red, in the case of pure lead salt solution, to yellow in the presence of the respective salts. The precipitation in presence of different salts is quantitative, when the concentration (gms. per 100 c c.) in each case does not exceed the amount stated below:—1 gm. for ammonium acetate, 15 gms. for potassium nitrate, 8 gms. for sodium acetate, and 4 gms. for ammonium nitrate.

The precipitate having the composition Pb_5O_7, $3H_2O$ is quite stable even when dried at 180°. Excess of hydrogen peroxide has somewhat dissolving action on the precipitate and changes it into lead hydroxide. It is soluble in excess of caustic alkalis but insoluble in ammonium hydroxide. Excess of alkali and ammonium salts has also got a solvent action. Hence in actual estimation of lead by this method, the volume of the solution should be kept such that the concentration of the ammonium salt formed during the process does not exceed the values specified above and also an excess of ammonia should in each case be employed.

The present method can claim advantage over the recently described method of Spacu and Dick (*Z. anal. Chem.*, 1927, **72**, 289) in the fact that it is possible to estimate lead in a solution containing larger amounts of the same and even when it is present as an acetate.

Further work on the subject specially regarding the nature of the precipitates in presence of the nitrates and acetates of alkalis and ammonia and the possibility of separating and estimating lead in presence of other metals is in progress.

Experimental.

The best condition for obtaining the crystalline precipitate of Pb_5O_7, $3H_2O$ from lead nitrate or acetate solution is to add one or two drops of dilute nitric or acetic acid and then to dilute to a considerable volume with water, then 2 c c. of 3% hydrogen peroxide are added for nearly 0·1 g. of lead present in the solution, stirred well and finally 2 c c. of concentrated ammonia are added at a time for the same amount of lead. The mixture is stirred well and then on heating over water-bath for 20 minutes, stirring occasionally or on boiling for 5 to 7 minutes, it is allowed to settle. By this the flocculent and bulky precipitate as obtained in the cold changes to a scaly crystalline condition. The clear liquid over the precipitate is as far as possible decanted through a Jena glass silica-bed cruicible (3/5-7) fitted in a filtering flask and a slow suction is maintained by mouth during the filtration, care being taken that as little as possible of the precipitate comes on the bed of the crucible ; otherwise it clogs the pores of it and renders the filtration and washing of the precipitate difficult, thus causing much hindrance to the rapidity of the method. The precipitate is washed by decantation with 50 c.c. of warm water several times till the wash water is free from nitrate or acetate as the case may be. The whole of the precipitate is then transferred into the crucible with a little water, and finally the precipitate is washed with absolute alcohol and sucked well. The final washing with alcohol may be avoided, in that case the crucible with the precipitate is dried for a longer time (about an hour). The washed precipitate is then dried at 110^0-120^0 for half an hour and weighed. During the time of weighing it was observed that the precipitate slowly increased in weight ; probably this is due to the slow absorption of moisture by it. Hence the weighing should be finished within a minute or two.

For this, a second weight is taken after the usual heating and cooling. With higher amounts of lead as in Experiment No. 15, 100 c.c. of warm water are used each time for washing by decantation. In this case some 8 to 10 times' washing is required to free the precipitate from ammonium nitrate and also the precipitate takes a greater time for drying ; to be sure here, the heating, cooling and weighing are carried a third time.

Solutions of pure lead nitrate and acetate were prepared and their respective strengths were determined by the sulphate method. In the solutions lead was estimated according to the present method. The results of the analyses are tabulated below.

Results.

No.	Lead nitrate solution taken (c.c.)	C.c. of hydrogen peroxide added.	C.c. of conc. ammonia added.	Weight of the precipitate.	Found Pb cal from Pb_3O_7, $3H_2O$ Log $F\left(\frac{Pb}{Pb_3O_7,\ 3H_2O}\right)$ $=\bar{1}\cdot9354$.	Pb present (estimated by sulphate method).	% of error.
1	5	2	2	0·1163 g.	0·1002 g.	0·0995 g.	0·7
2	5	2	2	0·1160	0·09999	,,	0·5
3	5	2	2	0·1154	0·09945	,,	0·05
4	5	2	2	0·1164	0·1003	,,	0·8
5	5	2	2	0·1156	0·09963	,,	0·13
6	5	2	2	0·1150	0·0991	,,	0·4
7	21	8	8	0·4872	0·4199	0·4179	0·5
8	1	1	1	0·0228	0·01964	0·0199	1·3
9	1	1	1	0·0232	0·01999	,,	0·45
10	1	1	1	0·0235	0·02025	,,	1·75
11	2	1	1	0·0460	0·03965	0·0398	0·4
12	2	2	2	0·0463	0·03990	,,	0·25
13	3	2	2	0·0696	0·05998	0·0597	0·47
14	5	2	2	0·1205	0·1039	0·1035	0·38
15	50	20	20	1·2010	1·035	1·035	0·0
16	5 (acetate)	2	2	0·1037	0·08935	0·08937	0·02
17	10 ,,	4	4	0·2068	0·1782	0·1787	0·3

The results as shown in the table are evidently satisfactory. The method is excellent where the amount of lead present gives the weight of precipitate in the first decimal place of the grammes.

In conclusion we are much thankful to Principal Dr. D. N. Mallik and Mr. J. C. Das, Professor of Chemistry, Carmichael College, Rangpur, for their kind permission and giving us every facility to conduct this work in the Chemical Laboratory of the College, and also to Professor P. R. Ray of the University College of Science. Calcutta, for the kindness he has shown in fully revising the paper.

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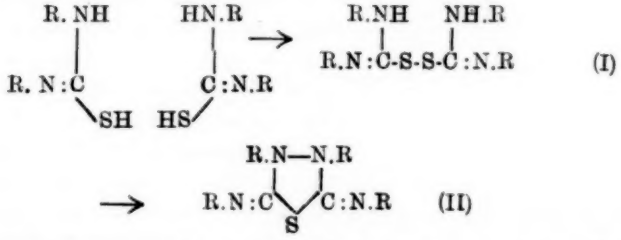
Studies on Oxidation. Part II. Action of Ferric Chloride and Hydrogen Peroxide on Symmetrical and Unsymmetrical Di-substituted Thiocarbamides and the Synthesis of Thiodiazoles.

By Tarinikanta Chakrabarti and Satishchandra De.

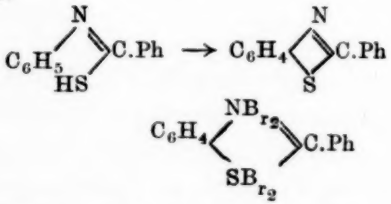
In Part I of this series it has been shewn by one of us (*J. Indian Chem. Soc.*, 1928, **5**, 269) that thiodiazoles of different types can be obtained by the action of suitable oxidising agents on aldehyde and ketone-thiosemicarbazones. In the present paper our object is to extend the work in this direction by preparing a few more thiodiazoles by oxidising the various diarylthiocarbamides, the course of reaction being represented according to the following scheme:



that is, the thiocarbamide is probably first oxidised to a disulphide (I) which is not possible to isolate and this then undergoes further oxidation to yield the thiodiazole (II) with the separation of one atom of sulphur.

Hector (*Ber.*, 1889, **22**, 1177; 1890, **23**, 357) has already described the preparation of certain thiodiazoles obtained from the action of oxidising agents on the monosubstituted arylthiocarbamides on the lines postulated above. Further, Hugershoff (*Ber.*, 1903, **36**, 3121) and later on, Hunter (*J. Chem. Soc.*, 1925, **127** 2023, 2270; etc.) in a series of papers have recorded the interesting observations on the conversion of symmetrical diarylthiocarbamides through the agency of bromine into arylaminobenzothiazoles by way of perbromides, which on treatment with sulphurous acid is rapidly reduced, the bromine being eliminated as hydrogen bromide and the free base

formed. The following example will illustrate the mechanism of the reaction:



Here also the action of bromine may in the first phase be regarded as an oxidising effect removing two atoms of hydrogen from the thiocarbamide, *viz.* one atom from the benzene nucleus and the other from the thiol group; and in the second phase the unsaturated compound takes up more bromine to form perbromide.

All these curious observations made it a point of interest to investigate into the action of oxidising agents on the disubstituted arylthiocarbamides and thus to extend the reaction to the preparation of thiodiazole derivatives (II) and, therefore, the oxidising action of hydrogen peroxide and of ferric chloride on the diarylthiocarbamides in water or alcohol was studied. Under conditions analogous to these employed in the previous cases, symmetrical or asymmetrical diarylthiocarbamides readily passed into thiodiazole derivatives when hydrogen peroxide was used as the oxidising agent; but with ferric chloride the symmetrical diarylthiocarbamides were in most part decomposed to yield the respective mustard oils which were distilled and identified and in the original solutions were obtained guanidine derivatives together with tar and in no case the formation of the thiodiazoles could be traced. Consequently the action of ferric chloride on the thiocarbamides has not been described in the experimental part. Thus hydrogen peroxide is found to be very suitable in oxidising these compounds as this method gives a tolerably good yield and gives no difficulty in isolating the thiodiazoles.

Experimental.

2:5-*Diphenylimido*-3:4-*diphenyl*-1:3:4-*thiodiazole* (Formula II, R=Ph).

Symmetrical diphenylthiourea (5 g.) was gently boiled with 50 c. c. of alcohol under reflux in a flask on the water-bath until it went into solution. The flask was then taken out and fitted with a cork through which was inserted a separating funnel which contained

3·5 gms. (a little more than one atom of oxygen required for one molecule of thiocarbamide) of perhydrol diluted with ten times of water. After the solution in the flask had sufficiently cooled and crystals had just begun to separate from the solution, the perhydrol solution was slowly added from the separating funnel with continuous shaking. Heat was evolved and sulphur precipitated. Some of the alcohol was then boiled off, sulphur removed and from the solution crystals separated on long standing. These were collected and recrystallised from rectified spirit; m. p 228°-230°: (Found: N, 13·44; C, 74·51; H, 4·94; S, 7·83. $C_{26}H_{20}N_4S$ requires N, 13·33; C, 74·28; H, 4·76; and S, 7·62 per cent.).

2:5-*Di* p-*tolylimido*-3:4-*di*-p-*tolyl*-1:3:4-*thiodiazole*.—It was prepared as before using sym-di-*p*-tolylthiocarbamide with the difference that in this case the reaction product was thrown out of solution within a few minutes as a white amorphous substance. It was boiled under reflux for 15 minutes more with the addition of alcohol and filtered hot. The substance was then crystallised thrice from acetic acid; m. p 261°: (Found: N, 11·34. $C_{30}H_{28}N_4S$ requires N, 11·76 per cent.).

2:5-*Di*-o-*tolylimido*-3:4-*di*-o-*tolyl*-1:3:4-*thiodiazole*.—It was prepared from symmetrical di-*o*-tolylthiocarbamide and perhydrol in exactly the same way as the above compound. The white substance obtained was crystallised from acetic acid when it melted at 249°. (Found: N, 11·59. $C_{30}H_{28}N_4S$ requires N, 11·76 per cent.).

2:5-*Di*-m-*xylylimino*-3:4-*di*-m-*xylyl*-1:3:4-*thiodiazole*.—With the slow progress of reaction which began on warming the mixture of the thiocarbamide and perhydrol, the sym.-*m*-xylylthiocarbamide went into solution and after a short time the reaction produet was precipitated as a white crystalline powder. This was crystallised thrice from alcohol (large volume); m. p. 247°. (Found: N, 10·67. $C_{34}H_{36}N_4S$ requires N, 10·53 per cent.).

2:5-*Di*-α-*naphthylimino*-3:4-*di*-α-*naphthyl*-1:3:4-*thiodiazole*.—To a hot suspension of sym-di-α-naphthylthiocarbamide in alcohol was added perhydrol when no reaction took place. The mixture was, therefore, boiled under reflux for a few minutes when the reaction commenced as was shown by a sudden change of appearance of the thiocarbamide. Heating was discontinued shortly after this (too much of heating should be avoided as the solid is thereby changed into a tarry mass) and the reaction product was crystallised thrice from acetic acid and obtained as a white substance which melted to a dark

liquid at 285°. (Found: N, 9·14. $C_{42}H_{28}N_4S$ requires N, 9·03 per cent.).

2:5-*Di*-β-*naphthylimino*-3: 4-*di*-β-*naphthyl*-1:3:4-*thiodiazole*.—It was obtained from sym.-β:β-dinaphthylthiocarbamide and perhydrol by a method similar to that described in the case of the α-compound as a white substance which after crystallisation from acetic acid shrinks and changes in colour at 268° and melts at 288° to a dark liquid. (Found: N, 9·17. $C_{42}H_{28}N_4S$ requires N, 9·03 per cent.).

2:5-*Di*-(*phenylmethylamino*)-1:3.4-*thiodiazole*.—Prepared as before from unsym-phenylmethylthiocarbamide in alcohol, the reaction product did not separate from the solution which, however, became a little turbid owing to the separation of sulphur. The solution was, therefore, concentrated to about one-forth of its volume but still no precipitate was obtained. The solution was then exposed to air to allow the alcohol to evaporate when a substance was left behind in the form of a syrupy liquid. This was dissolved in ether, and as the ether evaporated off the reaction product separated in a solid crystalline form. It was then crystallised from a mixture of alcohol and water; m. p. 94°. (Found: N, 18·98. $C_{16}H_{16}N_4S$ requires N, 18·92 per cent.).

2:5-*Di*-(*phenylethylamino*)-1:3:4-*thiodiazole*.—The oily product obtained from unsym.-phenylethyl-thiocarbamide and perhydrol according to the foregoing method was dissolved in ether from which it was obtained as a white crystalline mass. This was collected and recrystallised from dilute spirit; m. p. 107°-109°. (Found: N, 17·41. $C_{16}H_{20}N_4S$ requires N, 17·28 per cent.).

2:5-*Di*-(*diphenylamino*-)-1:3:4-*thiodiazole*.—Oxidised as before unsym-diphenylthiocarbamide gradually dissolved forming a clear solution from which the reaction product was thrown out of solution as a yellowish precipitate. The mixture was allowed to cool, filtered and the residue crystallised thrice from alcohol; m. p. 155°. (Found: N, 13·49. $C_{26}H_{20}N_4S$ requires N, 13·33 per cent.).

We wish to express our gratitude and thankfulness to Prof. J. C. Ghose and Dr. P. C. Guha for their encouragement during the progress of this investigation.

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A Theory of Colour on the Basis of Molecular Strain. Part V. Absorption Spectra and Dissociation Constants of Organic Salts of Violuric Acid.

By Narendranath Ghatak and Sikhibhushan Dutt.

The present paper is the outcome of an attempt to study the phenomenon of colour in the case of violurates and violuric acid from the point of view of colour put forward by one of the present authors (Dutt, *J. Chem. Soc.*, 1926, **129**, 1171; *J. Indian Chem. Soc.*, 1927, **4**, 99), and thereby to throw more light on the question of the constitution of violuric acid and violurates in solution about which there is a longstanding controversy.

Though much work has been done with the alkali salts of violuric acid (Hartley, *J. Chem. Soc.*, 1905, **87**, 1797; Hantzsch, *J. Chem. Soc.*, 1909, **96**, *i*, 333; Meek and Watson, *J. Chem. Soc.*, 1916, **109**, 544) from the point of view of colour and chemical constitution, the organic salts of violuric acid mentioned in this paper (most of which are new compounds) have never before been made a study of from the same point of view. These salts of violuric acid are derived from very weak bases, some of which for example have the basicity constants of the order of 10^{-11}, but all the same their solutions have colour which is in no way less intense than that shown by the solutions of alkali violurates. This goes to show that the high basic nature of the base is not very essential to produce the colour phenomenon. It may, as will be shown later on, intensify the colour to some extent. It should also be noted that in the case of alkali violurates, the salt being a combination of strong base and weak acid, we have

$$\underset{}{MA} + \underset{}{H_2O} = \underset{\text{Largely dissociated}}{M{\cdot}OH} + \underset{\text{Practically undissociated}}{HA}$$

where MA denotes the salt of violuric acid with the alkali base M·OH, and HA the violuric acid. Therefore it can be shown that

$$\frac{K_w}{K_a} = \frac{x^2}{(1-x)v}$$

where x = the number of molecules of salt hydrolysed in v litres of water, $K_w = 1{\cdot}2 \times 10^{-14}$ and K_a = the dissociation constant of the

acid. It will be noted that the amount of hydrolysis is dependent on the dilution and changes from one dilution to another. Consequently in the cases of alkali salts of violuric acid this defect of hydrolysis is present, and for a comparative study of optical properties this cannot be neglected or in any way eliminated. Hence the results of previous workers, who have not taken into account this hydrolysis, cannot be accepted without some caution.

Since the violurates recorded in this paper are derived from weak organic bases, this defect is eliminated. The salts being the products of very weak bases and a weak acid, the amount of hydrolysis is given by

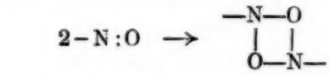
$$\frac{x^2}{(1-x)^2} = \frac{K_w}{K_a.K_b}$$

where x = the number of molecules hydrolysed in v litres of water, $K_w = 1{\cdot}2 \times 10^{-14}$ and K_a and K_b = the dissociation constants of the acid and base respectively. Since the above expression is free from v, it is apparent that the amount of hydrolysis is independent of the dilution. Moreover the factor K_b being almost the same in most of the cases investigated, the amount of hydrolysis is practically the same in all the cases. Consequently in a comparative study of their optical effect, it is eliminated. Therefore these violurates suited our purpose better than the alkali violurates.

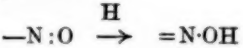
Magnaninni (*Gazzetta*, 1894, **24**, I, 48) has shown that violuric acid has an affinity constant $K = \cdot00272$. In aqueous solution containing a gram molecule of the acid in 256 litres, about 8% of the molecules are present dissociated into their ions. Such a solution is colourless or at best has a very light colour, and the ions according to Ostwald and Donnan should be practically colourless. The same author measured the colour of solutions of sodium, potassium and ammonium violurates at various dilutions and came to the conclusion that the absorption is directly proportional to the number of gram molecules of salt present and not to the number of free ions. Furthermore he showed that the addition of potassium nitrate to the solution sufficient to diminish the electrolytic dissociation by 25% has no effect on the absorption. These experiments of Magnaninni leave the conclusions of Ostwald and Donnan very doubtful. Another fact which goes against their hypothesis is that violuric acid and in fact most oximido compounds when heated exhibit abnormally large coefficients of conductivity and also large

dissociation constants, but this phenomenon finds no parallel change in colour (Guinchant, *J. Chem. Soc.*, 1899, **76**, *i*, 781; Hantzsch, *J. Chem. Soc.*, 1909, **96**, *i*, 331).

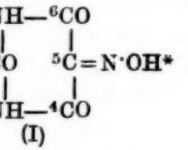
These facts clearly point to the fact that the colour phenomenon is not intimately connected with the electrolytic dissociation of violurates, and suggest that the substance in solution must have undergone some fundamental change in constitution so as to produce these interesting optical properties. It has been shown by one of the present authors (Dutt, *loc. cit.*) that a double bond between a nitrogen and an oxygen atom produces the greatest effect on the colour and absorption spectra of organic compounds, and consequently the true nitroso compounds are highly coloured. On account of the great molecular strain existing in all these substances, they are as a matter of fact very unstable and consequently undergo oxidation and reduction with the greatest ease, with formation of nitro- and amino-compounds with comparatively smaller degree of molecular strain. Many of the nitroso compounds tend to lose their internal strain by formation of bimolecular ring compounds:



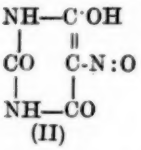
But if the nitroso group is in a molecule containing a labile hydrogen atom, it automatically rearranges itself to a condition of less strain in the following manner:



A typical example of this nature is *iso*nitroso-malonyl-urea or violuric acid, which is usually represented by the formula (I)



(I)



(II)

and since this compound is a fairly strong acid of monobasic character, it is probably quite reasonable to assume such a structure for violuric acid with the hydrogen atom marked by asterisk to be replaceable by metals.

This formula is known as the 'oximino-ketonic' formula, and besides this there is also an alternative nitroso-enolic structure (II) which is equally capable of formation.

This latter structure represents violuric acid as containing the highly strained nitroso group, and if such a form be correct then we should expect violuric acid to be a highly coloured substance. While on the other hand, if the oximino-ketonic form be correct, then violuric acid should not have any colour at all, or at best only a pale yellow colour.

Now as a matter of fact we find that violuric acid is almost colourless in the solid state, while in aqueous solution it has a pink colour, the absorption spectra of which has been determined by a number of chemists (Donnan and Schneider, *J. Chem. Soc.*, 1895, **95**, 956; Morton and Tipping, *J. Chem. Soc.*, 1925, **127**, 2514) and has been found to have a maxima at about wave-length 5300λ. From this it is apparent that violuric acid must have a configuration which is tautomeric between (I) and (II) according to the existing circumstances. Thus in the solid state violuric acid should have the comparatively little strained configuration (I), while in solution the more highly strained structure should be present. But on account of the lightness of the hydrogen atom and the consequent ease with which it is transferred from one position to another, this tautomerism between the two forms of violuric acid should be very rapid, and the full colour that is expected of such a structure as (II) would not be developed.

This state of things becomes somewhat modified when an alkali metal salt is taken instead of violuric acid. Under such circumstances on account of the greater load and consequent difficulties of tautomerism from one form to another, the more highly strained nitroso-enolic form will be more stable whenever its existence is possible. The —CO— group in position 6 is really the residue of a carboxyl, and still retains its carboxylic character in a modified form on account of the proximity of the -NH- group, whose basic character it has more than neutralised. Therefore when such a -CO- enolises by the transference of a labile hydrogen atom, it becomes as much acidic in character as a carboxyl, and therefore more so than an -N.OH group. Hence it can be easily seen that in an aqueous solution of violuric acid the latter exists mainly in form (I) with only a small proportion of form (II). But as soon as an alkali like sodium hydroxide is added to the solution, in order to neutralise the highly alkaline character of the latter, the original weakly acidic oximino-ketonic form of violuric acid has to tautomerise to the more acidic nitroso-enolic form. And in this form it becomes fixed by

salt formation with sodium hydroxide. But in this type of tautomerism the original slightly strained molecule becomes more highly strained with the result that its absorption spectra become shifted more towards the red end of the spectrum. Hence from this it can be easily seen that the stronger the basic character of the alkali used, the greater will be the transformation into the nitroso-enolic form, and the intensity of colour will be correspondingly greater. This has been actually proved by the investigations of Hantzsch and his co-workers (*Ber.*, 1909, **42**, 1066) who have shown that the greater the basic nature of the alkali or alkaline earth used in the salt formation with violuric acid, the greater is the intensity of the colour of the corresponding salt thus formed.

Apart from the consideration of the constitution of violuric acid it will be clear from the results recorded in this paper, that the greater the basic character of the organic base, the greater in general is the production of colour by salt formation with violuric acid. Though it has not yet been found possible to derive any direct mathematical relationship between the dissociation constants and absorption spectra of the organic salts of violuric acid, it may be said in general that as the dissociation increases, the absorption also increases though to a comparatively small extent.

Experimental.

Most of the organic salts of violuric acid described in this paper were prepared by mixing equimolecular proportions of the acid and the organic base in alcoholic solution and on evaporating at the ordinary temperature, large well-developed crystals were obtained. These were then recrystallised from water or dilute alcohol. All the violurates without exception crystallise in fine long needles with silky lustre. In physical appearance they are either violet, pink or blue with occasional specimens of an orange colour. All of them dissolve in water or organic solvents like alcohol or acetone with various shades of pink colour. The salts do not contain any water of crystallisation and are exceedingly pure, as is confirmed by a number of analytical data given at the end of this paper. Most of them undergo decomposition when heated to about 85°, and the same thing happens when they are exposed to atmospheric conditions for a long time.

The absorption spectra and the dissociation constants were determined by the ordinary methods, taking particular care to secure highly accurate results. The results are summarised in the following table:

Absorption Spectra and Dissociation Constants of Organic Violurates.

(V = Violurate.)

Name of the salt.	Appearance.	Colour in aqueous solution.	Dissociation constant.	Molecular conductivity at N/128 dilution.	Absorption maxima (A) at N/128 dilution.	Analytical data (theoretical values in brackets).
1. Violuric acid ...	Colourless needles.	Pale pink	·2164	·2415 × 10³	5305	—
2. Ammonium V ...	Violet ,,	Violet-red	·9262	·1049 × 10³	5832	—
3. Methylamine V ...	,, ,,	,,	·9016	·7547 × 10²	5782	N = 29·4 (29·7%).
4. Dimethylamine V ...	Violet blue ,,	Deep-pink	·9140	·8091 × 10³	5793	—
5. Trimethylamine V ...	Blue ,,	,, ,,	·9177	·7375 × 10³	5712	N = 25·7 (25·9%).
6. Ethylamine V ...	Scarlet ,,	,, ,,	·9104	·7257 × 10³	5697	N = 27·4 (27·7%).
7. Diethylamine V ...	Violet ,,	,, ,,	·8887	·7266 × 10³	5690	—
8. *n*-Propylamine V ...	,, ,,	,, ,,	·8878	·7235 × 10³	5532	N = 25·7 (25·9%).
9. *n*-Butylamine V ...	Pink ,,	Pink	·8753	·7147 × 10³	5532	—

10. Aniline V	... Blue	,,	,,	·7382	·3498 × 10^{5}	5673	N = 22·0 (22·4%).
11. *o*-Toluidine V	... Pink	,,	,,	·6390	·3023 × 10^{5}	5626	N = 21·0 (21·2%).
12. *m*-Toluidine V	... Greenish blue	,,	,,	·5575	·3635 × 10^{5}	5678	N = 20·8 (21·2%).
13. *p*-Toluidine V	... Violet	,,	,,	·6679	·3878 × 10^{5}	5684	—
14. Methylaniline V	... ,,	,,	,,	·5321	·3475 × 10^{5}	5654	N = 21·1 (21·2%).
15. Ethylaniline V	... ,,	,,	,,	·5249	·3382 × 10^{5}	5654	—
16. *o*-Phenylenediamine V	... ,,	,,	Red	·4427	·6089 × 10^{5}	5694	N = 26·1 (26·5%).
17. *p*-Phenylenediamine V	... Pink	,,	,,	·5338	·3527 × 10^{5}	5694	—
18. *α*-Naphthylamine V	... ,,	,,	Pale pink	·2810	·2321 × 10^{5}	5499	—
19. *β*-Naphthylamine V	... ,,	,,	,, ,,	—	·3197 × 10^{5} (N/512)	5222	N = 18·6 (18·7%)
20. Pyridine V	... Orange	,,	Pink	·5810	·4471 × 10^{5}	5692	N = 23·7 (23·6%)
21. Piperidine V	... Blue	,,	Deep pink	·8551	·6970 × 10^{5}	5697	—
22. Quinoline V	... Orange	,,	Pink	·5746	·3969 × 10^{5}	5683	—
23. *α*-Picoline V	... Pink needles		,,	·5885	·4029 × 10^{5}	5692	N = 22·2 (22·4%)

Absorption Spectra and Dissociation Constants of Organic Violurates (contd.)

(V = Violurate.)

Name of the salt.	Appearance.	Colour in aqueous solution.	Dissociation constant.	Molecular conductivity at N/128 dilution.	Absorption maxima (λ) at N/128 dilution.	Analytical data (theoretical values in brackets.)
24. Nicotine V	... Blue ,,	Deep pink	·6639	·6152 × 10³	5695	N = 23·1 (23·5%).
25. Morphine V	... ,, ,,	,, ,,	·7513	·4820 × 10³	5691	—
26. Brucine V	... Violet ,,	,, ,,	·7273	·5151 × 10³	5679	—
27. Strychnine V	... Blue ,,	,, ,,	·7721	·5289 × 10³	5660	N = 14·0 (14·3%).
28. Cinchonine V	... Pink ,,	,, ,,	·6821	·5002 × 10³	5557	N = 15·2 (15·5%).
29. Quinine V	... Violet ,,	,, ,,	·6086	·4106 × 10³	5537	—
30. Cocaine V	... Blue ,,	,, ,,	·7655	·4525 × 10³	5674	N = 12·1 (12·2%)

Our best thanks are due to Prof. N. R. Dhar, D.Sc., for lending us a precision conductivity apparatus and also for the kind interest he has taken during the progress of the work.

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The Dielectric Constant of Methylene Chloride and Methylene Bromide.

By P. C. Mahanti and D. N. Sen-Gupta.

It is a well-known experimental fact that the dielectric constant of molecules having symmetrical structures is independent of temperature whereas the polar molecules having asymetric constitution indicate a diminution of the dielectric constant with rise in temperature.

The theoretical aspect of this phenomenon was investigated by Debye (*Phys. Zeit.*, 1921, **13**, 97), J. J. Thomson (*Phil. Mag.*, 1924, **27**, 757), and Gans (*Ann. Physik*, 1921, **64**, vi, 481) on classical consideration. Pauli (*Zeit. Physik*, 1921, **6**, 319), and Manneback (*Phys. Zeit.*, 1926, **27**, 563; 1927, **28**, 72) treated the same from the standpoint of classical quantum theory and wave-mechanics.

Considering that the molecules of gases and vapours are polarised in an electric field and that the polarisation field acting on the molecules is isotropic in character, Debye deduced the following expression for the dielectric constant of molecules which are unaffected by temperature,

$$\frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} \cdot 4N\gamma \qquad \ldots \qquad \ldots \quad (1)$$

where

ϵ = Dielectric constant;

M = Molecular weight;

ρ = Density;

N = Avogadro's number;

γ = Polarisability of the molecule.

For molecules whose dielectric constant is affected by variation in temperature, Debye assumed that they develop a permanent dipole having a fixed direction with reference to the molecule. Assuming that the distribution of molecules is regulated by the well known Boltzmann—Maxwell distribution law with temperature, the contribution of these permanent dipole moments to the dielectric constant can be expressed by the expression

$$\frac{4\pi}{v} \cdot \frac{\mu^2 N}{KT} \quad \ldots \quad \ldots \quad (2)$$

where μ = Moment of the dipole;

K = Boltzmann constant;

T = Absolute temperature.

Thus the complete expression for the dielectric constant is

$$\frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{\rho} = \frac{4\pi N}{3}\left(v + \frac{\mu^2}{3kT} \right) \quad \ldots \quad (3)$$

Since in gases ϵ differs by a very small amount from unity, we can put $\epsilon+2=3$.

$$\text{Hence} \quad \frac{\epsilon-1}{\rho} \cdot MT = 4\pi N\gamma T + \frac{4\pi N}{3k} \cdot \mu^2 \quad \ldots \quad \ldots \quad (4)$$

Further assuming that gases and vapours in unsaturated state obey the simple gas laws and noting that

$$\frac{\rho_o}{M} = \frac{1}{22{\cdot}4 \times 10^3} \text{ gm.},$$

$$\text{we get} \quad \frac{(\epsilon-1)\, P_o T^2}{P} = av T + b\mu^2 \quad \ldots \quad \ldots \quad (5)$$

$$\text{where } a = \frac{4\pi N_o T}{22{\cdot}4 \times 10^3} \qquad b = \frac{4\pi N T_o}{3k \times 22{\cdot}4 \times 10^3}$$

The expression (5) giving a direct method of ascertaining the magnitude of the polarisability ν of the molecule as well as the magnitude of the dipole moment μ in the molecule.

Thus drawing a graph with T and $\frac{(\epsilon-1)\, P_o T^2}{P}$ as x and y axes,

the slope of the line will be the value of $a\nu$ and the intercept at the origin of co-ordinates will give the value of $b\mu^2$.

On the basis of the above formula, Zahn (*Phys. Rev.*, 1924, **23**, 345), Watson (*Proc. Roy. Soc.*, 1927, **117**, 43), Braunmühl (*Phys. Zeit.*, 1927, **28**, 141), Sänger (*Phys. Zeit.*, 1926, **27**, 556), and Maske *Phys. Zeit.*, 1927, **28**, 553) have determined the dielectric constant and dipole moment of several gases and vapours. Rieger (*Ann. Physik*, 1919, **59**, viii, 753) and Zahn and Smyth (*J. Amer. Chem. Soc.*, 1925, **47**, 2501) together also investigated into the relation between the unsaturated bonds of organic molecules and their dielectric constant.

The nature of change of the polarisability and dipole moments of some of the ethyl and methyl halides has been investigated by the present authors (*Indian J. Phys.*, 1928, **3**, 181). It is seen that the polarisability of these halides increases as we pass from the chlorides to the iodides whereas the permanent dipole moment diminishes. In the present paper the authors propose to detremine the polarisability and the dipole moment of the symmetrical molecule CH_4 when two of its hydrogen atoms are replaced by halogen atoms.

The dipole moment of CH_2Cl_2 has already been determined by Sänger (*loc. cit.*) by a method differing in technique from that of the present authors, who, therefore, have repeated his observations on CH_2Cl_2 and measured the polarisability and dipole moment of CH_2Br_2, thus getting these values for the two methylene halides under the same arrangement which the authors have developed.

Experimental.

The experimental arrangement is the same as has been adopted in a previous investigation (*loc. cit.*). *viz.*, that of the heterodyne beat method when two oscillating circuits, as shown in Figure 1, of

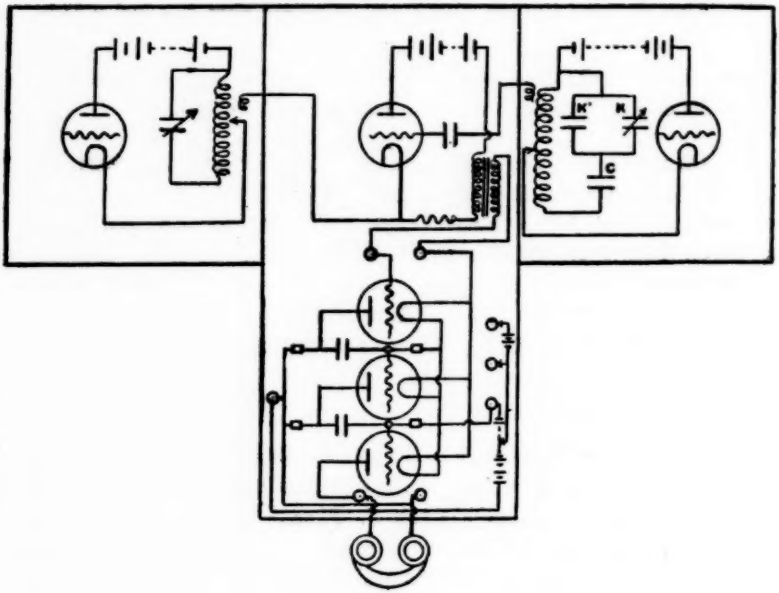

Fig. 1.

frequencies $1{\cdot}5 \times 10^6$ and $1{\cdot}501024 \times 10^6$ respectively are loosely coupled to produce a beat tone of 1024 frequency. The beat tone is adjusted in unison with a valve maintained tuning fork of 1024 frequency. The experimental gas condenser c is put in series with a standard precision variable vernier condenser K, which is in parallel with a fixed condenser, K', of the Dubilier type. The methods of adjustment and the calibration of the condensers used are described in detail in the above paper.

The chemicals used were brought from Schuchardt.

Results.

TABLE I.

Methylene Chloride, b.p. 41°.

T°.	$(\epsilon-1)760$	$\frac{(\epsilon-1)P_0T^2}{P}$
303·0	·007076	649
332·5	·005920	655
390·0	·004369	664
426·0	·003684	672

Methylene Bromide, b. p. 81°.

T°.	$(\epsilon-1)760$	$\frac{(\epsilon-1)P_0T^2}{P}$
322·0	·008808	912
357·0	·007248	924
388·0	·006177	930
420·0	·005329	940

TABLE II.

Vapour.	$(\epsilon-1)$.	$\mu \times 10^{18}$.
CH_2Cl_2	·0006890	1·621
CH_2Br_2	·0009947	1·914

A graph showing the relation between $\frac{(\epsilon-1)P_0T^2}{P}$ and T^0 is given in Fig. 2.

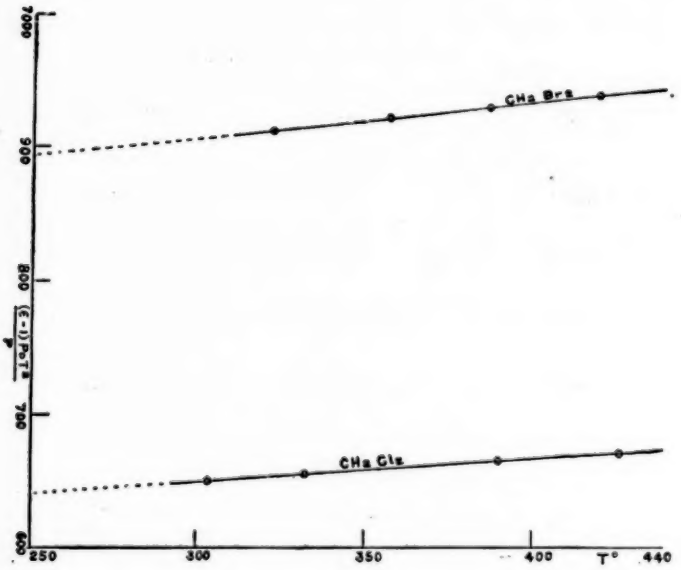

Fig. 2.

Discussion.

It has been pointed out in a previous paper (*loc. cit.*) that a symmetrical molecule of the type of CH_4 and C_2H_6 get their symmetry disturbed by the substitution of a single atom of hydrogen by a halogen atom. It was further pointed out that the polarisability of the molecule is increased when Br is substituted for Cl and I is substituted for Br. On the other hand the dipole moment of RCl is greater than that of RBr and that of RBr greater than that of RI, R standing for the CH_4 or C_2H_6 group.

The nature of polar molecules has been investigated by Born Debye and others from the behaviour of ions in solution and of

crystalline solids composed of solid ions in aggregation. One can assume that polar molecules are composed of positive and negative ions held together by electrostatic forces and there may be a transfer of one or more electrons from one atom to another. In the majority of polar molecules it is reasonable to picture the model as composed of ions whose individual atoms retain their own electronic orbits and the attractive force between the ions is balanced by the force of repulsion between their electronic shells. Lewis and Langmuir from a large number of instances consider the model as that of atoms consisting of rigid shell of eight electrons and the outer valency electrons forming a link which keeps the stability of the molecules. Fajans and Joos (*Zeit. Physik*, 1924, **23**, 1) investigated the polarisability of the electronic shell from the viewpoint of dispersion. Born and Heisenberg (*Zeit. Physik*, 1924, **23**, 388) treated the same subject in the case of alkali halides in solution and considered that this molecular polarisability can be deduced from the consideration of the deformation of the electron orbits according to the spectroscopic standpoint. The molecular structure has their electronic shells participating in a fashion as to form an inert gas configuration. The polarisability as deduced from dispersion measurements of Wasastijerna (*Comm. Fernn.*, 1913, **1**, 7) of dilute solutions of the salts is in fair agreement with the data from the rare gases.

To form a mental picture of the formation of the molecules of the type having a positively charged organic radicle and a negatively charged halogen ion, it is easy to conceive that they will attract each other and the formation of a stable molecule requires a force of repulsion at short distance to balance this force of attraction. The origin of this force of repulsion is well known in the case of simple polar halides like HCl where the H^+ nucleus enters a region in which the outermost electron no longer attracts it so strongly and the repulsive force between the nuclei balances the nett attractive force of the electron swarm and H^+ ion thus forming the stable HCl molecule. This hypothesis is tenable in view of the small size of H^+ ion.

In the case of organic halides formed of the CH_3^+ and Cl^- ions however, such a pentration of CH_3^+ inside the electronic boundary of Cl^- would involve an apparently hopeless distortion of both the electron orbits. Hence it would be more reasonable to assume that each retains its own electron orbits and the electron spheres would

not interpenetrate some other source of repulsion is to be sought to explain the formation of such a stable molecule. Debye (*Zeit. Physik*, 1921, **22**, 302) has suggested an origin of this force. He first discusses the formation of a negative ion and calls attention to the fact that if a free electron is brought near an atom, *i.e.*, an electron rotating in an orbit about a nucleus, the free electron will tend to execute forced oscillations with the period of the orbital electron, which would slow down on its approach to the free electron and the time average of the repulsive force will be increased. The same considerations would lead to similar repulsion acting when an atom approaches an atom or a positively charged iron approaches an atom.

Now let us suppose that when Cl^- ion approaches a positive radicle such as CH_3^+, the loosely bound electron of the negative ion would take up an orbit encircling both the Cl atom and the CH_3^+ radicle. The repulsive force between the Cl nucleus and the nuclei of the CH_3^+ together with the repulsive force of the orbital electron of Cl^- and the orbital electron of CH_3^+ would balance the attractive force of the electron swarm of Cl^- and the CH_3^+ radicle and the stable CH_3Cl molecule is formed.

In the case of the molecules CH_2Cl_2 and CH_2Br_2, the two loosely bound electrons of the negatively charged halogen ions would encircle the system and the above considered mutual forces would lead to the formation of the molecules.

It is further known that CH_4 can be regarded as having the structure of a symmetrical tetrahedron with C atom at its centre of gravity (Dennison, *Astro. J.*, 1925, **62**, 84). The CH_2Cl_2 molecule may be regarded as a distorted tetrahedron with the Cl atoms at its two corners. Due to the interaction of the electronic orbits the orbits of Cl atoms as well as that of CH_2^{++} will be distorted. These distortions will develop moments in the two Cl atoms as well as in the CH_2^{++} ion. The direction of the moments in the two Cl atoms will be mutually inclined to each other and the moment of CH_2^{++} will be making equal angles with the direction of the moments in each Cl atom. The moments of Cl atoms will however partly neutralise each other due to their inclinations and the nett permanent moment of the molecule is the resultant of the moment of the CH_2^{++} ion and the resolved part of the moments of the Cl atoms operating in the opposite direction.

When Br is substituted in place of Cl, the Br nuclei come in closer proximity to the C-nucleus and owing to the larger nuclear charge of Br they are mutually separated from each other to a larger extent than in the case of Cl atoms. The two electrons surrounding the system are more rigidly bound to it than in the case of CH_2Cl_2. Their orbits are thus less distorted and hence CH_2Br_2 has a larger polarisability than CH_2Cl_2. This increase of polarisability evidently indicates a greater cohesive force acting inside the molecule and the boiling point of CH_2Br_2 is therefore higher than that of CH_2Cl_2. This greater polarisability also accounts for the smaller interatomic forces to form the molecule leading to low stability. Hence CH_2Cl_2 is more stable than CH_2Br_2.

Now when we consider the permanent dipole moment of CH_2-Br_2, we notice that the two Br atoms are more inclined to each other than in the case of Cl atoms and the resultant of the resolved part of their moments acting in the direction opposite to that of the moment developed in the CH_2^{++} ion will be less than in the case of Cl atoms. The nett dipole moment of CH_2Br_2 is thus greater than that of CH_2Cl_2.

The authors expect a still higher polarisability and a greater dipole moment in the case of CH_2I_2 but technical difficulties stand in the way to its measurement, partly because the vapour pressure of CH_2I_2 is very low at the room temperature and also that the CH_2I_2 decomposes at ordinary temperatures under normal pressure. The boiling point of CH_2I_2 is about 130°. With the present arrangement only those liquids that have boiling points below 100° can be studied.

Our best thanks are due to Prof. P. N. Ghosh for suggesting the theoretical aspect of the phenomena and for his continued help and guidance during the course of the investigation.

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On the Nature of the Time-Dilution Curves in Some Hemolytic Systems.

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In three previous papers (Sen and Basu, *Ind. Jour. Med. Research*, 1928, **15**,, 581 ; This *Journal*, 1928, **5**, 1 ; Sen and Sen, This *Journal*, 1928, **5**, 261) we have studied certain aspects of hemolysis in presence of serum. While thus studying the hemolysis by bile salts, we were confronted with certain results of a very peculiar type in the time-dilution curves of some of these hemolytes which required further investigation. The present paper is a continuation of our previous studies, and contains results of some determinations of time-dilution curves with several hemolytic substances. Many determinations of these time-dilution curves with different hemolytes and blood corpuscles have been made from time to time, and among these we can mention the works of MacLean and Hutchinson (*Biochem. J.*, 1909, **4**, 369) and Ponder (*Proc. Roy. Soc.*, 1922, **93B**, 86 ; 1923, **95B**, 42 ; 1926, **99B**, 465 ; 1927, **101B**, 205). Our interest in this subject was aroused by some observations of MacLean and Hutchinson. These authors studied the hemolysis of sheep corpuscles by the sodium salts of glycocholic and choleic acids and came to the conclusion that these substances are capable of producing hemolysis in the ordinary way when strong doses are used, but exhibit marked peculiarities when present in considerably weaker amounts. It was found that under similar conditions the same hemolytic effect can be produced in a given time by widely divergent amounts of the salts. Between these two points lies what may be termed a more or less neutral zone, in which the hemolysis is very considerably delayed depending on the relative amounts of the hemolytic agent employed. Ponder in recent times has confirmed this result with glycocholate, but according to him sodium taurocholate does not give any peculiar result of this sort, and the time-dilution curve is of a much simpler nature. In view of the fact that taurocholic acid is closely related to the other acids

studied by MacLean and Hutchinson, it is surprising that the salt of this acid would behave in an entirely different manner. Also, since no explanation of the so-called "hemolytic paradox" was offered by MacLean and Hutchinson, it seemed desirable to study the subject anew in order to find out a suitable explanation for the peculiarities observed. Some time-dilution curves have therefore been obtained with different hemolytes, and this paper contains part of the results.

Experimental.

The method of experimentation is in principle the same as given in the previous papers. Since the determination of the end-point is a colourimetric one, particular care was taken to select glass tubes of equal transparency, the bore and the thickness being the same. The mixing of the corpuscle with the hemolyte was finished within 10 seconds, and the tube was then allowed to stand in a uniform temperature, and generally was not at all disturbed except in those cases where the time necessary for complete hemolysis was very high. An interesting fact in connection with the hemolysis by some hemolytes used in this paper is that when the hemolyte and the corpuscles are mixed together as soon as hemolysis starts, the reaction appears to be very rapid and in many cases near about 90% of the cells are hemolysed within a comparatively short period. The first stage in hemolysis thus seems to be of the nature of an autocatalytic reaction. The remaining amounts of the corpuscles however take an appreciable amount of time for hemolysis, and there appears to be a retardation when the last stage in complete hemolysis is reached. When observed visually, the last trace of turbidity of the corpuscle and hemolyte mixture takes a fairly long time to disappear completely unless the hemolyte is in great excess.

The experiments given in the present paper were all done with sheep's erythrocytes. Defibrinated corpuscles were repeatedly washed by normal saline in order to free them from serum, and were then suspended in normal saline to give a concentration of 5 per cent. In the actual experiments, 1 c.c. of this cell suspension was used in every case unless otherwise mentioned. The total volume of the suspension *plus* hemolyte was always made up to 5 c.c. by the previous addition of normal saline if

necessary. Among the hemolytes used, potassium oleate and saponin were obtained from Kahlbaum, sodium taurocholate from Merck, and the solutions were freshly prepared to prevent any change in the nature of these substances in solution on standing. Special care was taken with the taurocholate which was prepared only 10 minutes before the actual experiment was carried out. The taurocholate concentration was 3 per cent, and it may be stated that the concentration of the hemolyte is almost the same as used by MacLean and Hutchinson with choleate and glycocholate, the corpuscles being in both cases of sheep of identical concentration The concentration of taurocholate used by Ponder was however low. All the hemolytes were dissolved in normal saline. Two different samples of sheep corpuscles have been used, and for one experiment a slightly hemolysed sample of erythrocyte suspension was taken. The temperature was 32°, and the corpuscles, when not in use, were kept in an ice-chest, the temperature being always below 5°.

The first table contains the results of oleate hemolysis. A stock solution of one per cent potassium oleate was prepared and from this a 1 in 10,000 oleate was prepared.

TABLE I.

Oleate in c.c.	Final conc.	Time of complete hemolysis in minutes,	Remarks.
0·5	1/100,000	>130	No hemolysis in these times.
0·8	1/62,000	>130	
1·0	1/50,000	115	
1·2	1/41,000	72	
1·5	1/33,330	35	
1·8	1/27,770	18	
2·0	1/25,000	10	
2·5	1/20,000	5	
3·0	1/16,660	2	

In Table II are given a few data with different amount of corpuscles. Oleate concentration has been 2 c.c. of 1 in 10,000.

TABLE II.

Amount of cells in c.c. ...	1·0	1·5	2·0
Time for complete hemolysis in minutes	10	30	100

In Table III are given the data on taurocholate hemolysis. The peculiar time periods are to be noted.

TABLE III.

Taurocholate in c.c.	Final conc.	Time for hemolysis in minutes.
0·1	1/1666	26
0·5	1/333	8
1·	1/166	16
1·5	1/111	11
2·0	1/83·3	27½
2·5	1/66·6	42
3·0	1/55·6	27
3·5	1/47·6	5

In Table IV are given some data of alkali hemolysis. Caustic soda N/10 was prepared in normal saline.

TABLE IV.

NaOH in c.c.	Final conc.	Time for hemolysis in minutes.	Remarks.
0·1	N/500	> 135	Only slight hemolysis.
0·3	N/166·6	66	
0·5	N/100	31	
0·7	N/71·4	19	
1·0	N/50	12	
1·3	N/38·5	9	
1·5	N/33·3	7½	
2·0	N/25	4½	

In Table V are given some data on acid hemolysis. Hydrochloric acid N/50 was prepared in saline and this solution was used in the experiments.

TABLE V.

HCl in c.c.	Final conc.	Time for hemolysis in minutes.	Remarks.
0·1	N/2500	> 45	No hemolysis.
0·2	N/1250	45	About 40 per cent. hemolysis in this time.
0·4	N/625	25	
0·6	N/416·6	14	
0·8	N/312·5	9	
1·0	N/250	6	

In studying this acid hemolysis, it was observed that not only hemolysis took place but along with it the hemoglobin turned brown and finally a sedimentation was formed. In order to determine the correct end-point in these cases, a simultaneous count of the R.B.C. was made under the microscope. It was observed that when the end-point in hemolysis was reached, there was practically no R.B.C. in the microscopic field, but even one or two minutes before the time of complete hemolysis, large number of R.B.C. were to be observed under the microscope.

In Table VI some data are given of the effect of alkali on oleate hemolysis. The object was to find out if there was any retardation of hemolysis. Several previous authors have found out this (Ponder, *loc. cit.*), but when actually doing the experiments, some peculiar results have been obtained which, it seems, have not been observed by any one before. The corpuscles were slightly hemolysed and hence a fresh determination of the time-dilution curve with pure oleate was also made. The concentration of oleate was 1 in 10,000.

TABLE VI.

Oleate pure c.c.	Time of hemolysis.	Oleate + 0·1c.c. N/10 NaOH.	Time of hemolysis.
1·0	100	1·0	45
1·2	68	1·2	36
1·5	34	1·5	24
1·8	14	1·8	23
2·0	11	2·0	22
2·2	9	2·2	19

The data given in Table VI are interesting. When the concentration of oleate is low, alkali accelerates the hemolysis, but when the oleate concentration is high, alkali retards the hemolytic effect of oleate. When observation is made on the actual progress of hemolysis in the tubes, a curious thing is observed. With the same concentrations of oleate, hemolysis always starts first in those tubes which contain alkali, but when oleate concentration is comparatively higher, pure oleate hemolysis ultimately gets faster than hemolysis by the mixture of oleate and alkali. With lower concentrations of oleate however mixed hemolytes have a better action. In view of this surprising fact, it was decided to repeat the experiment with a fresh sample of corpuscles because the earlier sample had become a little aged, and a few corpuscles were already laked. In Table VII these results are given. The oleate was freshly prepared, and the corpuscle concentration was the same as before. The concentration of oleate was 1 in 10,000.

TABLE VII.

Oleate pure c.c.	Time for hemolysis.	Oleate + 0·1 c.c. N/10 NaOH.	Time for hemolysis.
1·0	> 120	1·0	74
1·2	62	1·2	55
1·5	27	1·5	41
1·8	12	1·8	36
2·0	9	2·0	27
2·5	7	–	–

A perusal of the data given in Table VII will immediately show that these results entirely confirm those given in Table VI. Consequently we have to resume that the phenomenon is true and hence an explanation has to be found for these interesting, though apparently abnormal, effects of alkali in oleate hemolysis.

Since we have found certain abnormalities in oleate and taurocholate hemolysis, it was now thought desirable to investigate more fully the case of saponin hemolysis which, according to several

authors, does not show any abnormality. In Table VIII the results are given. The saponin concentration as given below is 1 in 10,000, but in actual experimentation, sometimes a 1 in 1,000 solution has been used. The solutions were prepared from a stock solution of 1 in 100 which was also freshly prepared.

TABLE VIII.

Saponin.	Final conc.	Time of hemolysis.	Remarks.
0·5	1/100,000	> 5½ hours	No hemolysis at all.
1·0	1/50,000	> 5½ hours	About 10% hemolysis.
1·5	1/33,333	> 5½ hours	About 20% hemolysis.
2·0	1/25,000	> 5½ hours	About 40% hemolysis.
2·5	1/20,000	> 5½ hours	About 60% hemolysis.
3·0	1/16,666	> 5½ hours	About 80% hemolysis.
3·5	1/14,286	258	
4·0	1/12,500	230	
4·5	1/11,111	71	
5·0	1/10,000	50	
5·5	1/9090	43	
6·0	1/8333	35	
6·5	1/7692	30	
8·0	1/6250	16	
10·0	1/5000	10	
12·0	1/4166	4	
15·0	1/3333	3	
20·0	1/2500	1½	

In Table IX the effect of alkali on saponin hemolysis is shown

TABLE IX.

Saponin + 0·1 c.c. N/10-NaOH.	Time of hemolysis.	Saponin pure c.c.	Time of hemolysis.
5·0	156	5·0	50
8·0	73	8·0	12
10·0	56	10·0	10
12·0	50	12·0	4
15·0	21	15·0	3

The results in Table VIII show that no abnormality is observed in the saponin series, and Table IX shows that alkali has always a retarding influence and the series is therefore unlike that of oleate. For this reason it was thought desirable to repeat our previous work on taurocholate hemolysis with this new sample of corpuscles. The taurocholate solution was freshly prepared and was 3 per cent. strong. The data in Table X show the results. For comparative purposes, the effect of alkali is also shown in this table.

TABLE X.

Taurocholate in c.c.	Time of hemolysis.	Taurocholate + 0·1 c.c. NaOH.	Time.
0·1	14	0·1	No hymolysis in any of the tubes in 35 minutes. Complete inhibition within this period.
0·5	2	0·5	
1·0	10	1·0	
1·5	10½	1·5	
2·0	14	2·0	
2·5	14½		
3·0	10½		
3·5	4		

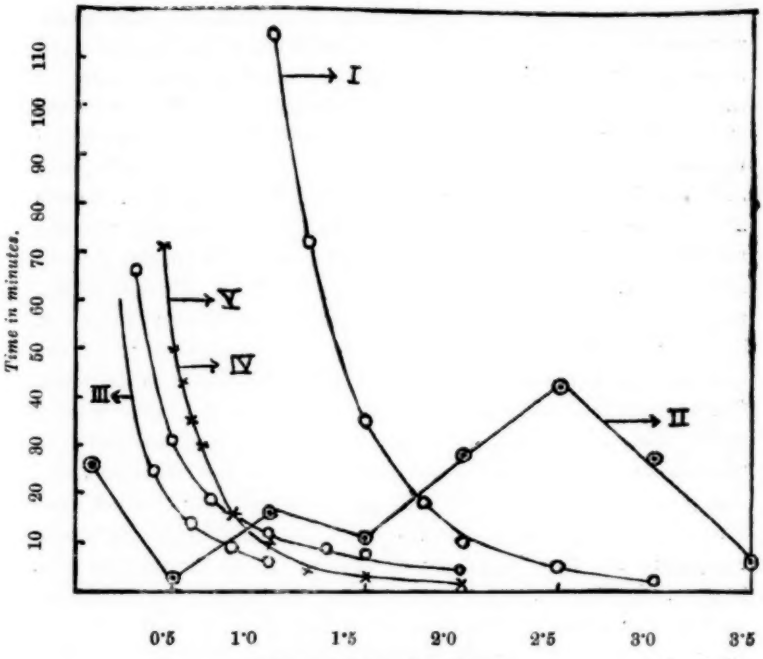
The results of Table X thus entirely confirm those given in Table III.

Discussion.

The results presented in the previous pages may be discussed primarily from two points of view, namely whether the time-dilution curves with different hemolytes are normal or abnormal, and secondly whether the effect of alkali is the same in all the cases. In Fig.

I the time dilution curves of the different hemolytes are plotted in

FIG. I.



Amount of hemolytes in c.c.

Saponin in terms of 1 in 1000.

I = Oleate; II = Taurocholate; III = Hydrochloric acid; IV = Caustic soda; V = Saponin.

the same paper which would thus give a comparative representation of the nature of the curves. For obvious reasons, the time and concentrations cannot be plotted according to the same scale with different hemolytes, and so these curves do not show the efficiency of these hemolysers on sheep's corpuscles. Also saponin is included in these curves though the experiments were made with a different sample of cells. The point of interest in these curves is that no abnormality is to be noticed in the case of hemolytes saponin, caustic soda, potassium oleate and hydrochloric acid, but there is a marked peculiarity when sodium taurocholate is used. This agrees with the type of results obtained by MacLean and Hutchinson, but

does not agree with those obtained by Ponder or Yeager (*J. Gen. Physiol.*, 1928, **11**, 779). According to our results sodium taurocholate hemolysis is quite analogous to the glycocholate hemolysis. It is not possible to state definitely why Ponder's results are different, but a suggestion may be made that Ponder's experiments were carried out with much lower concentrations of the hemolyte and corpuscles and this may have an important bearing on the nature of the time-dilution curve of sodium taurocholate. Similarly if we look at the other end of the series, namely with higher concentrations of the taurocholate, it will be apparent from a study of the results given in Tables III and X, that when the taurocholate concentration exceeds 2·5 c.c. per 5 c. c. of the mixture, the fall in the amounts of time necessary for complete hemolysis is regular and there appears to be no abnormality. Hence if experiments are carried out only within this range of hemolyte concentration, a normal time-dilution curve can be obtained. We believe that with very low concentrations of the taurocholate, a similar normal time-dilution curve is to be expected. Our experimental observation will also explain another fact. Ponder found that glycocholate is a very weak hemolyte as compared to taurocholate, but we have found previously (Sen and Basu, *loc. cit.*) that glycocholate is a much stronger hemolyte than taurocholate. This difference probably depends upon the fact that we have been comparing the two hemolytes in concentrations far different from that used by Ponder. It is quite possible that in the concentrations we had been using, the comparison has been made in that portion of the curves where the action of taurocholate was about the minimum but the effect of glycocholate was near about the maximum. This would show that glycocholate is the stronger hemolytic agent. In the experiments of Ponder however the concentrations of the comparing hemolytes may have been such that the conditions are just the reverse of that of ours, and hence an entirely different result was obtained. The problem of hemolysis by the salts of the complex bile acids is so complicated that it appears that divergent results are only to be expected at present till a more thorough investigation is made. Thus our experience with glycocholate hemolysis leads us to the belief that this particular hemolysis which is known to give an abnormal series and shows the so-called "hemolytic paradox" of MacLean and Hutchinson can be made to give a normal time-dilution curve if a suitable and comparatively high concentration range is chosen. This view is also strengthened by a perusal

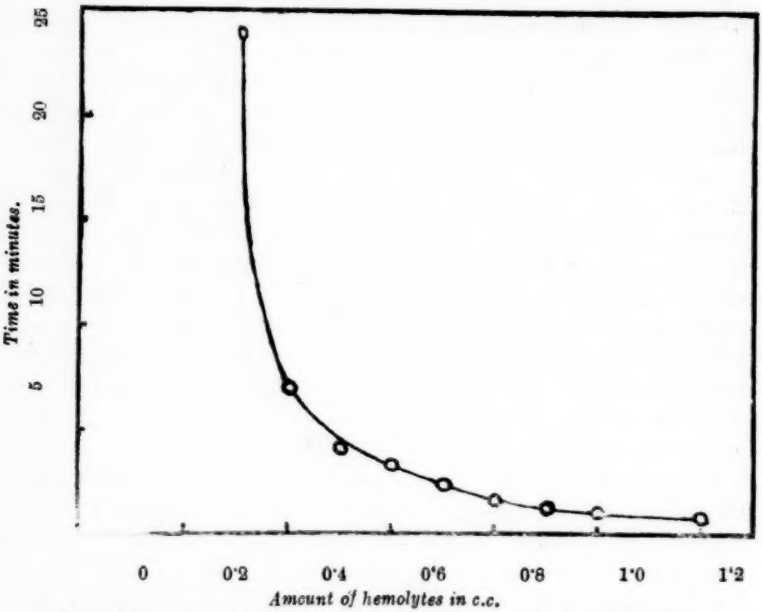
of the actual results obtained by MacLean and Hutchinson with sodium cholalate, choleate and glycocholate. It is observed from their data that with sodium cholalate, the time-dilution curve up to a concentration of 0·1 c.c. of M/10-cholalate in a 5 c.c. mixture gives a normal series. Again from a concentration of 0·8 c.c. up to 3 c.c. of the cholalate, the time-dilution curve is perfectly normal. The abnormality is only to be noticed between the concentration range 0·1 and 0·8 c.c. Similarly with sodium choleate, the time-dilution curve is normal up to a concentration of 0·1 c.c. M/10 of the salt and then again between the range 1·0 and 3·0 c.c. but is abnormal between the range 0·1 and 1·0 c.c. of the hemolyte. With sodium glycocholate the curve is normal up to 0·08 c.c. and then again from 0·5 to 3·0 c.c. These results therefore support our conclusion arrived experimentally that an abnormality in taurocholate hemolysis can be expected and that the difference in our results from that of some other workers is to be attributed to different experimental conditions. The assumption that we may expect a normal series in the time-dilution curve of taurocholate when the concentration of the hemolyte is low has also been experimentally confirmed by us and the results are given in Table XI. In order to use a low concentration of the hemolyte, we were obliged to use a low concentration of the cells. In the following table, 1 c.c. of an one per cent suspension prepared by diluting the previously used corpuscles in saline has been used. The taurocholate concentration is 0·3 per cent. The cell suspension is the same as used in Tables VIII to X. In the final mixture the concentration of the cells is 1/5th of that used in other tables.

TABLE XI.

Taurocholate in c.c.	Final conc.	Time of hemolysis in minutes.
0·1	1/16666	>2 hours
0·2	1/8333	>2 hours
0·3	1/5555	24
0·4	1/4166	7
0·5	1/3333	4
0·6	1/2777	3 mins. and 15 secs.
0·7	1/2381	2 mins. and 20 ,,
0·8	1/2083	1 min. and 30 ,,
0·9	1/1851	1 min. and 7 ,,
1·0	1/1666	0 min. and 55 ,,
1·2	1/1389	0 min. and 40 ,,

From this table and from Fig. II it will be immediately observed

FIG. II.



Time-dilution curve of sodium taurocholate in low concentrations with small amount of erythrocytes.

that there is no abnormality in the time-dilution curve within the particular concentration range of the hemolyte and the cell suspension. Thus the result of some investigators who have found a normal series with taurocholate is confirmed for a particular experimental condition. But taking the complete data of taurocholate hemolysis into consideration, we come to the conclusion that sodium taurocholate also may show the "hemolytic paradox" and in this respect is quite analogous to other salts of the bile acids. So far as other hemolytes studied in this paper are concerned, all of them appear to be normal, but some more experiments are being tried with the oleate.

The second interesting point is that of the effect of alkali on the hemolytic systems. In an earlier paper (Sen and Basu) it was shown that for some concentrations of OH ions, an inhibitory effect on hemolysis is to be expected, which is found to be a fact so far a saponin or taurocholate hemolysis is concerned. With oleate however, the peculiar result has been obtained that alkali acts as a

retarder of hemolysis when higher concentrations of oleate are used, but acts as an accelerator when comparatively lower amounts of oleate are used. We are at present unable to give an explanation of this behaviour, and the existence of the hemolytic paradox remains also unexplained, but we are continuing our experiments in these lines.

Summary.

(1) Time-dilution curves of hemolysis have been obtained with hydrochloric acid, caustic soda, saponin, potassium oleate and sodium taurocholate and sheep's erythrocytes.

(2) It is found that taurocholate gives an abnormal time-dilution curve, but other hemolytes show a normal series within the particular concentration range studied.

(3) It is shown that the so-called hemolytic paradox can be observed with taurocholate also when the concentration range of the hemolyte used is fairly wide. It is pointed out that the variation in the nature of the results of taurocholate hemolysis found in this paper from that of some other workers is probably due to the fact they have used a lower concentration of the hemolyte and corpuscles. Incidentally it has been emphasised that the actual concentrations used in the hemolytic systems may greatly influence the nature of the time-dilution curves.

(4) It has been observed in oleate hemolysis that the effect of small amount of alkali is twofold. At lower concentrations of oleate, alkali has an accelerating effect on hemolysis, but with higher concentrations of oleate, an inhibitory action is observed. The amount of alkali is however such that no visible action is noticeable when it is present alone within the experimental period.

(5) With saponin or taurocholate, alkali has a uniform retarding action. This confirms the result of previous workers and is in line with the mechanism of hemolysis discussed in a previous paper.

(6) Sodium glycocholate may have either a greater or lower hemolytic action than sodium taurocholate depending on the particular concentration range of the salts and the corpuscle concentration in which the comparison is made.

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Variations of the Electrical Charge of Colloidal Particles. Part III. The Influence of Non-electrolytes on the Cataphoretic Speed of Colloidal Particles and on the Adsorption of Ions by Colloidal Particles as indicated by such Measurements.

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In continuation of previous measurements (*J. Indian Chem. Soc.*, 1924, **2**, 296; *ibid*, 1927, **4**, 493) the cataphoretic speed of colloidal particles of arsenious sulphide as influenced by the addition of some non-electrolytes has been studied. Also the effect of hydrochloric acid and potassium chloride on the electrical condition of the particles has been studied in the presence of varying quantities of ethyl and methyl alcohols. Apart from their bearing on the theories which have been put forward to explain the process of coagulation these measurements have considerable interest of their own but a full discussion must await further investigation because our conceptions as to the nature of the so-called double-layer, the influence of non-electrolytes on the adsorption of ions and other related topics are yet unsatisfactory.

Experimental.

Preparation of the Arsenious Sulphide Sol.

The sol was prepared by mixing equal volumes of conductivity water saturated with hydrogen sulphide and a solution of arsenious oxide prepared by diluting a saturated solution with an equal volume of water and then passing a current of hydrogen sulphide for a definite time such that a slight excess of arsenious oxide is still left. A current of hydrogen was next passed till the hydrosol was found free from hydrogen sulphide on being tested with lead acetate.

The sol was kept wrapped up with black paper in a dark place. The apparatus and method developed by one of us (*Proc. Roy. Soc.*, 1923, **103A**, 102) have been used. The same cataphoretic tube was used during this investigation. The tube had only two side tubes and the effective distance between them was found to be 4·2 cms. for both directions. The temperature of the thermostat was $35 \pm 0{\cdot}05°C$. The rates of migration per second per volt/cm. multiplied 10^5 times have been expressed after making corrections for the changes in viscosity and assuming that of water to be unity. The addition of non-electrolytes has been found to make reliable measurements more difficult as the boundary becomes sensitive to slight changes in the composition of the upper liquid. Taking necessary precautions it is possible to get results reproducible within $\pm 2\%$. The error involved in reading the position of the boundary increases at high concentrations of the non-electrolyte.

The upper liquid used was an equally conducting hydrochloric acid solution to which the non-electrolyte and the electrolyte, if any, were added in the same proportion as that in which they were present in the solution.

Results.

Table I.

Arsenious Sulphide Sol[1] *and Methyl Alcohol.*

% of methyl alcohol by vol.	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity × 10^5.
0 (pure sol)	62·99	59·57	61·28	1·018	62·40
2½	56·45	53·33	54·89	1·048	57·54
5	45·63	45·63	45·63	1·091	49·82
10	29·09	33·98 (?)	31·54	1·155	36·43
15	25·64	26·75	26·20	1·242	32·55

[1] The non-electrolyte added replaces an equal volume of water.

TABLE II.

Arsenious Sulphide Sol and Ethyl Alcohol.

% of ethyl alcohol by vol.	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity × 10^5.
0 (pure sol)	62·99	59·57	61·28	1·018	62·40
2½	55·45	55·46	55·45	1·062	58·90
5	51·52	47·39	49·49	1·126	55·72
10	41·45	41·55	41·50	1·258	52·20

TABLE III.

Arsenious Sulphide Sol and Urea.

% of urea by weight (gms. in 100 c.c.).	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity × 10^5.
0 (pure sol)	62·99	59·57	61·28	1·018	62·40
2½	55·08	55·19	55·11	1·043	57·52
5	46·21	45·76	45·98	1·050	48·31
10	40·02	42·29	41·15	1·080	44·38

TABLE IV.

Arsenious Sulphide Sol and Cane Sugar.

Cane sugar (gms. in 100 c.c.)	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity × 10^5.
0 (pure sol)	64·25	60·08	62·16	1·015	63·07
2½	48·59	46·53	47·56	1·054	50·12
5	31·03	30·59	30·81	1·119	34·49
10	24·81	26·56	25·83	1·263	32·64

TABLE V.

Arsenious Sulphide Sol and Acetone.

% of acetone by volume.	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity × 10^5.
0 (pure sol.)	64·25	60·08	62·16	1·014	63·07
2½	52·23	54·24	53·24	1·041	55·40
5	45·51	45·44	45·47	1·084	49·32
10†	—	—	—	—	—

TABLE VI.

Arsenious Sulphide Sol and iso-*Butyl alcohol.*

% of *iso*-butyl alcohol (by volume).	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity × 10^5.
0	64·25	60·08	62·16	1·016	63·07
2½	59·95	55·55	57·75	1·068	61·68

TABLE VII.

Arsenious Sulphide with Ethyl Alcohol and Potassium Chloride.

% of ethyl alcohol by volume.	Conc. of potassium chloride.	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity × 10^5.
0	0	60·70	61·56	61·13	1·020	62·38
0	·01 N	56·69	56·47	56·58	1·010	57·12
2½	,,	51·89	52·90	52·40	1 062	55·68
5	,,	46·18	46·68	46·43	1·121	52·07
10	,,	39·65	38·63	39·14	1·262	49·40
0	·02 N*	53·46	57·39	55·42	1·006	55·78
0	,, *	55·91	55·18	55·54	1·006	55·90
2½	,, *	49·42	49·46	49·44	1·068	52·68
5	,, *	41·79	41·75	43·75	1·140	49·91
10	,, *	35·57	35·61	35·59	1·272	45·29
0	·04 N	53·37	51·91	52·64	1·017	53·53
0	,,	52·87	52·72	52·80	1·017	53·69
2½	,,	52·48	51·66	52·07	1·066	55·55
5	,,	46·73	46·46	46·59	1·131	52·70
10	,,	40·24	40·91	40·57	1·203	48·80

† The boundary gets disturbed during the 'reverse' movement.

* The pure sol used in these measurements showed a rate of $63·07 \times 10^{-5}$ cm. per volt/cm.

TABLE VIII.

Arsenious Sulphide Sol with Methyl Alcohol and Potassium Chloride.

% of methyl alcohol by volume.	Conc. of potassium chloride.	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity $\times 10^5$.
0	0	67·57	63·37	65·47	1·020	66·81
0	0	64·60	63·71	64·15	1·020	65·46
0	·004 N†	59·35	59·18	59·26	1·023	60·64
2½	,, †	51·55	52·38	51·96	1·051	54·60
5	,, †	43·12	55·16	44·14	1·081	47·71
10	,, †	30·64	35·32	32·98	1·188	39·20
0	·01 N	56·69	56·47	56·58	1·010	57·12
2½	,,	54·90	56·70	55·80	1·042	58·15
5	,,	49·88	53·54	51·72	1·084	56·08
10	,,	40·99	41·04	41·01	1·160	47·60
0	·02 N	53·46	57·39	55·42	1·006	55·78
2½	,,	57·25	60·78	59·01	1·046	61·71
5	,,	52·49	54·54	53·51	1·076	57·60
10	,,	46·70	47·89	47·30	1·156	54·69
0	·04 N	52·87	52·72	52·80	1·017	53·69
2½	,,	60·03	61·69	60·86	1·066	64·91
5	,,	55·90	57·16	56·53	1·077	61·65
10	,,	44·76	51·34	48·05	1·171	56·29

† Measurements with ·004 N potassium chloride was carried with a different preparation of the hydrosol which gave a rate of migration (corrected for viscosity) of $66·27 \times 10^{-5}$.

TABLE IX.

Arsenious Sulphide Sol with Ethyl Alcohol and Hydrochloric Acid.

% of ethyl alcohol by volume.	Conc. of hydrochloric acid.	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity $\times 10^5$.
0	0	66·85	63·27	65·05	1·034	67·26
2½	0	55·45	55·46	55·45	1·062	58·90
5	0	51·52	47·39	49·49	1·126	55·73
0	·005 N	52·17	50·94	51·56	1·017	52·44
2½	,,	46·51	47·51	47·01	1·069	50·22
5	,,	41·37	42·72	42·04	1·121	47·14
0	·01 N	45·66	46·88	46·27	1·000	46·26
2½	,,	41·88	42·48	42·18	1·069	44·98
5	,,	37·02	37·54	37·28	1·113	41·52
0	·015 N	43·37	43·64	43·50	1·003	43·62
2½	,,	36·97	37·65	37·31	1·067	39·80
5	,,	30·46	31·84	31·15	1·131	35·24

TABLE X.

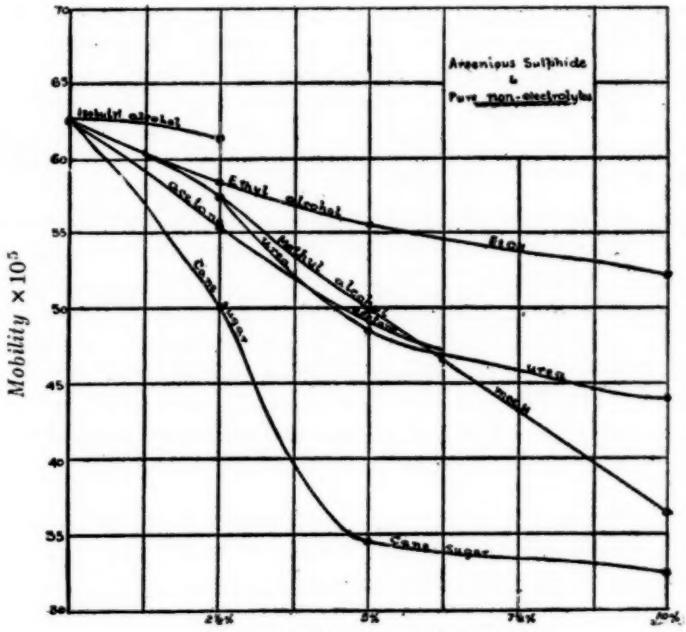
Arsenious Sulphide Sol with Methyl Alcohol and Hydrochloric Acid.

% of methyl alcohol by volume.	Conc. of hydrochloric acid.	Direct.	Reverse.	Mean.	Relative viscosity.	Rate of migration corrected for viscosity $\times 10^5$.
0	0	66·85	63·27	65·06	1·034	67·26
2½	0	56·45	53·83	54·89	1·045	57·54
5	0	47·73	45·79	46·76	1·091	51·04
0	·005 N	52·17	50·94	51·56	1·017	52·44
2½	,,	42·04	42·48	42·26	1·051	44·40
5	,,	37·14	36·64	36·89	1·081	39·87
0	·01 N	45·66	46·88	46·27	1·013	46·26
2½	,,	41·37	41·06	41·22	1·042	42·96
5	,,	37·16	36·03	36·59	1·083	39·67
0	·015 N	43·37	43·64	43·50	1·030	43·62
2½	,,	44·87	44·70	44·78	1·045	46·83
5	,,	40·04	41·06	40·55	1·076	43·64

Discussion.

(a) *The Effect of Non-electrolytes.*

The effect of non-electrolytes on the pure sol will be apparent from Figure (I). Cane-sugar which has very nearly the same effect



Concentration of non-electrolytes.

Fig. I.

on the dielctric constant of the medium at these concentrations as the other non-electrolytes decreases the cataphoretic speed (corrected for the alteration in viscosity) considerably and urea which slightly increases the dielectric constant also lowers the cataphoretic speed. According to Helmholtz u, the cataphoretic speed, ϕ the potential of the double layer, k, the dielectric constant and η the co-efficient of viscosity, are correlated by the following equation:—

$$u_0 = u\eta = \frac{k\phi}{4\pi} \qquad \ldots \quad (1)$$

The potential of the double layer is proportional to u_0/k where u_0 is

the cataphoretic speed after viscosity correction. It will be seen that an increase or a diminution of the dielectric constant on the addition of the non-electrolyte produces the same effect, namely, a lowering of the cataphoretic speed. It is apparent that the potential of the double layer is not determined by the change in the dielectric constant alone as Freundlich has assumed (*Kapillarchemie*, 1922, p. 638). After referring to equation (1) he states "Ein kleineres D bedingt ein kleineres u." Evidently he assumes the potential to be constant. He further (p. 337) discusses the relationship

$$e = \frac{\phi . k . r . (r+\delta)}{\delta} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where e is the density of the electrical charge on the surface, r is the radius of the particle and δ is the thickness of the double layer and points out that if the potential of the double layer remains constant and the dielectric constant decreases evidently, e the density of the charge should decrease, assuming that the thickness of the double layer is constant. There is no justification for considering that the potential will remain constant and the density of the charge will vary as the dielectric constant. This will be evident from Table XI to XIII below.

TABLE XI.

Methyl Alcohol.

% of Methyl alcohol	0	2½	5	10	15
k	80·4	78·75	77·5	75·0	72·8
u_o/k	·776	·730	·643	·486	·447

TABLE XII.

Cane Sugar.

% of cane sugar	0	2½	5	10
k	80·4	78·25	77·0	76·2
u_o/k	0·784	0·640	0·448	0·429

TABLE XIII.

Urea.

% of urea.	0	2½	5	10
k	80·4	80·0	81·0	83·25
u_0/k	0·776	0·720	0·596	0·533

The values k, obtained by interpolation from the data of Lattey (*Phil. Mag.*, 1921, **41**, 829) and of Harrington, (*Physical Rev.*, 1916, **8**, 581) have been used to determine the values of u_0/k given in the tables. It is obvious that the charge may be affected by other factors. There is evidence to show that a direct relationship exists between the amount of excess of adsorption of an ion of one sign and the rate of electro-osmotic or cataphoretic movements. It is therefore more rational to correlate the cataphoretic speed with the density of the charge on the surface of the particle. Lamb's equation has as its basis such a relation, if we assume that the facility of slip is not a function of the density of the charge. In Helmholtz's treatment also the fundamental factor determining the electrical force F is given by

$$F = H\rho \qquad (8)$$

where H is the intensity of the field and ρ is the volume density of the charge. The potential difference at the interface is introduced by Helmholtz through Poisson's relation for facilitating the solution of the hydrodynamic equations.

We see from equations (1) and (2) that e cannot vary directly as u_0 unless δ is constant. Further that a proportionality between u_0 and e (δ constant) does not necessarily imply that both e and u_0 vary as δ.

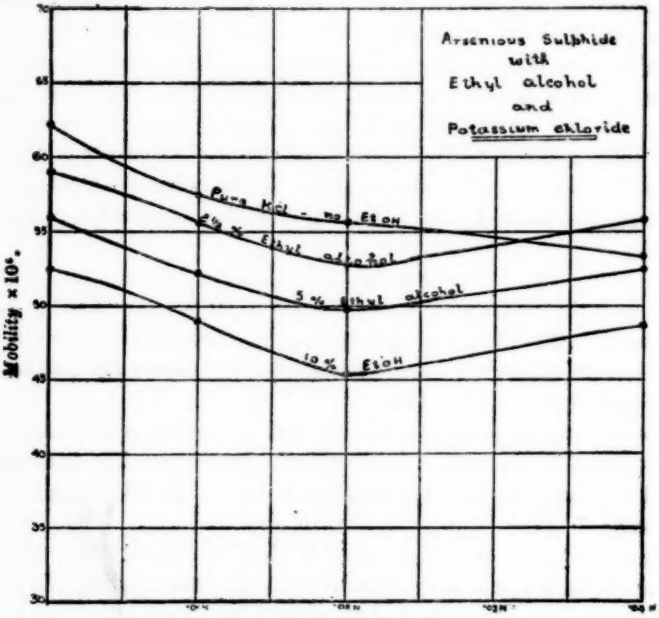
Theoretical considerations make it plausible that if δ be a function of k then it will vary directly as k. In that case u_0 cannot vary directly as k as assumed by Freundlich unless e is constant. The fact that all the non-electrolytes mentioned above lower the cataphoretic speed cannot therefore be explained from the above point of view. It is more plausible to explain our observations by assuming that either the density of the charge is changing or preferrably both the density and the thickness of the double layer are

changing. The great effect of cane sugar points to the conclusion that the variation in the density of the charge is the main factor. As our knowledge regarding the thickness of the double layer is insufficient it is not possible to discuss this question in greater detail. It is hoped that further investigations will enable us to form a clearer conception of the double layer.

(*b*) *Mixture of Non-electrolytes and Electrolytes.*

In this series of measurements the following broad peculiarities are noticeable.

Excluding the case of hydrochloric acid and ethyl alcohol on the addition of the non-electrolyte along with an electrolyte there is at first a marked decrease in speed but at higher concentrations the cataphoretic speed increases. In the case of potassium chloride at



Concentration of Electrolyte.

Fig. II.

all the three concentrations of ethyl alcohol the curves are nearly parallel and the minimum speed is observed at a concentration of ·02N of the electrolyte (Fig. II).

Methyl alcohol magnifies this tendency both as regards the initial decrease and the subsequent rise (Fig. III) and it is noticeable also for hydrochloric acid. The minimum in the presence of methyl

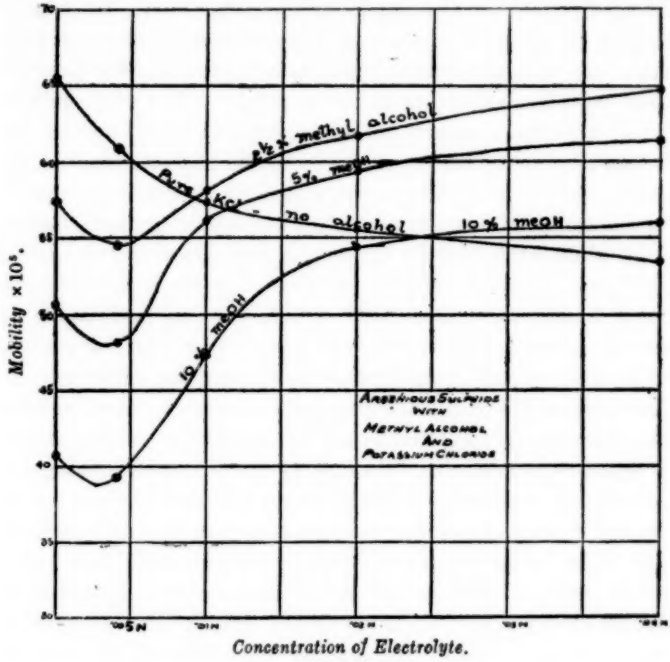


Fig. III.

alcohol and potassium chloride occurs at a much lower concentration. If we assume the validity of Helmholtz's equation in its usual form the cataphoretic speed u_0 is proportional to $K\phi$.

It is usually supposed that coagulation takes place at a constant critical potential which must be sufficiently low. We however find that on the addition of the non-electrolyte the speed rises considerably and in some case (*e.g.*, MeOH and hydrochloric acid) to a value greater than that of the original sol. Kruyt and Willigen *Z. physikal. Chem.*, 1927, **130**, 170) have attempted to account for coagulation by electrolytes when the electrolyte increases the cataphoretic speed on the basis that the dielectric constant k rises with increasing concentration of the electrolyte and hence the actual potential is less than that for the sol without electrolyte. In the case of 10 per cent. methyl alcohol and varying concentration of potassium chloride, the cataphoretic speed increases from a minimum

of about 39 to about 56, *i.e.*, by about 43 per cent. The dielectric constant of the mixture in the presence of 0·04N KCl must be supposed to be about 43 per cent. greater than that in the absence of the electrolyte in order to bring down the potential to its original value and if we assume that coagulation takes place at a lower potential (the critical potential) then the increase in the dielectric constant must be supposed to be much greater. It is most unlikely that the dielectric constant changes to such an extent and we conclude that there is no definite critical potential characteristic of the coagulation by an electrolyte as was suggested by Powis and quoted in the literature. Mukherjee and co-workers have repeatedly emphasised (*cf.* Mukherjee, *Thesis* ; Mukherjee and Chaudhury, *J. Indian Chem. Soc.*, 1925, **2**, 296; Mukherjee, Chaudhury and Rai-choudhury, *J. Indian Chem. Soc.*, 1927, **4**, 493) that this postulate is not warranted by facts. It thus appears that neither the cataphoretic speed nor the potential of the double layer calculated as above has a critical value at the coagulating concentration. A more probable explanation may be suggested on the following basis. The cataphoretic speed is a measure of the density of the electrical charge and the stability of the sol is dependent on the electrical charge in so far as electrical work must be done in displacing the free ions in the mobile layer when two particles come very near each other. This electrical work is determined by the number of ions displaced, the shape and extent of the surface affected (which also governs the distance through which these ions are displaced) and the dielectric constant of the medium. These considerations though more satisfactory than the conception of a critical potential are not however sufficient, for, as we find, coagulation occurs at a much higher cataphoretic speed than can possibly be explained by an increase in the dielectric constant resulting from the presence of the electrolyte. One way out of this difficulty would be on the basis that the cataphoretic speed is proportional to the product of the surface density and the thickness of the double layer and to assume that the thickness of the double layer depends on the dielectric constant so that the density of the charge is much smaller than that represented by the cataphoretic speed. An increase in the dielectric constant will also diminish the electrical work, other conditions remaining the same as an increase in the dielectric constant will have a two-fold effect and it may be that the nett electrical work will be less than that for the approach of two particles of the original sol.

As we have no reliable data on the dielectric constant of so highly conducting solutions these considerations are not very useful.

On the other hand we know that ethyl alcohol and methyl alcohol sensitises the sol as would appear from the following data, from a paper by Mukherjee, Chaudhury and Mukherjee (*J. Indian Chem. Soc.*, 1926, 3, 349).

TABLE XIV.

Arsenious Sulphide Sol.

Percentage concentration of ethyl alcohol.	Electrolyte concentration in normality. HCl	KCl	$AlCl_3$
0	0·03800	0·05944	0·0002184
2·5	0·03675	0·06064	0·0002146
5	0·03525	0·06301	0·0002146
10	0·03400	0·07055	0·0002109
15	0·03300	0·07847	0·0002109
25	0·03500	0·00618	0·0002033

TABLE XV.

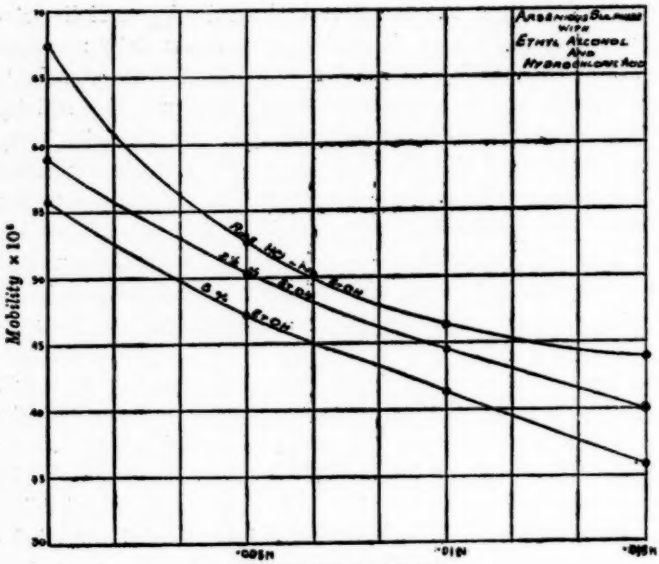
Percentage of methyl alcohol.	Electrolyte concentration in normality HCl	KCl	$AlCl_3$
0	0·04450	0·06024	0·0001995
2·5	0·04325	0·05909	0·0001957
5	0·04225	0·05863	0·0001920
10	0·04050	0·05707	0·0001882
15	0·03850	0·05470	0·0001770
25	0·03550	0·05070	0·0001581

The cataphoretic speed at an electrolyte concentration of ·04N-KCl decreases with increasing content of methyl alcohol but the cataphoretic speed at the same electrolyte concentration when no alcohol is added is in this case the least. While the increasing sensitisation with the increasing concentrations of methyl alcohol can be explained by the progressive diminution of the cataphoretic speed such an explanation is not possible for the case when no electrolyte is added, unless we assume that the dielectric constants of the alcohol-water mixtures are considerably greater in the presence of the electrolyte than that of the pure aqueous solution. It is not possible to lose sight of the fact that the coagulating concentration cannot be directly correlated either to the potential of the double layer or the cataphoretic speed without introducing a number of assumptions, the validity of which remains to be tested. It is therefore desirable to keep in view the possibility that specific forces of the nature of cohesion may be operating and these are affected by the adsorption of ions from the electrolyte and of the non-electrolyte. The observations of Bhattacharya in this laboratory show that the manner of variations of the cataphoretic speed with the concentration of potassium chloride is different depending on the method of preparation of the sol and its dilution, but the coagulating concentration does not show an equally complicated behaviour. It therefore seems probable that in addition to the effect of electrical work and cohesive forces stated above, we have to consider that the actual stable aggregation results from a simultaneous entrainment in the surface of contact, of an equivalent (or nearly equivalent) amount of the ions of opposite sign in the mobile layer. This idea is similar to that underlying Whetham's attempt at an explanation of the valency rule of Schulze.

From the foregoing the complex nature of the observations and the difficulties of explaining them on the basis of the theories in vogue at present are apparent. Similar difficulties stand in the way of accounting for the cataphoretic speed from the point of view of the adsorption of ions. Broadly speaking we notice that the rise in the cataphoretic speed at higher concentrations depends on both the nature of the cation and the non-electrolyte. The marked initial decrease in the presence of the non-electrolytes may be referred to a lowering of the dielectric constant and an increase in the adsorbability of the cation.

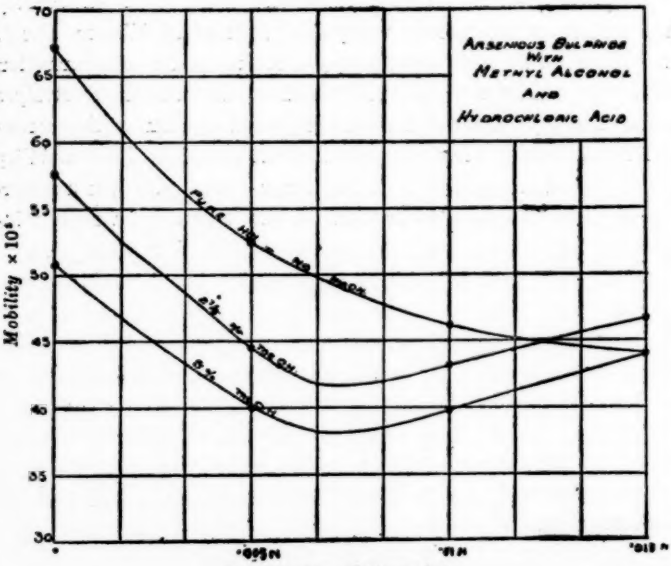
The non-electrolyte has an effect both on the degree of dissociation (osmotic coefficient) as determined from conductivity measurements and on the mobility of the ion. On theoretical grounds it appears probable that the osmotic coefficient (and not the activity coefficient) is the relevant factor in these cases. On Debye's theory from considerations of the electrical factor, the osmotic coefficient should decrease with the diminution in the dielectric constant and hence the osmotic coefficient should be the least for methyl alcohol and the greatest for water. It is well known that the mobilities diminish on the addition of alcohol and the percentage diminution is very high for small concentrations of the non-electrolyte.

The slope of the curve showing the initial decrease in charge will be much greater if we plot the osmotic coefficients instead of the stoichiometric concentration. On the basis of Mukherjee's theory of electrical adsorption this increased slope can be accounted for by the lower dielectric constant which would increase the adsorbability of the cation. There is no doubt as to this increase in the adsorbability if one also considers the lower mobility and makes corrections according to his equation. Now the diminution in the charge facilitates the primary adsorption of chlorine ions which have an affinity for the surface of the arsenious sulphide particles (*cf.* Weiser, Dhar). On the other hand the rate of increase of the actual concentration of the cation with the stoichiometric concentration of the electrolyte is slower in the presence of non-electrolytes on account of the stronger electrical forces. If we also consider the lowering of the mobility of the cation on the addition of these non-electrolytes it is not surprising that the primary adsorption of the anions soon rapidly increases and hence surpasses the progressively weaker adsorption of the cation. The initial lower speed may be taken to indicate a lower density of charge and consequently the repulsive forces exerted on the anions by the negatively charged surface is smaller. This would moreover increase the rate of adsorption of the anion. Apparently these effects will be more pronounced the higher the concentration of the non-electrolyte and the lower its dielectric constant. Moreover for the same anion the lower the adsorbability of the cation, the more pronounced will be these features (the initial drop and the subsequent rise).



Concentration of Electrolyte.

Fig. IV.



Concentration of Electrolyte.

Fig. V.

These conclusions are fairly borne out by the Figures IV and V. While this representation enables us to form a picture, subject to the limitations mentioned, there is one difficulty. The osmotic coefficient of the chlorine ions and its mobility are also smaller. Besides the lower dielectric constant will decrease the adsorption of chlorine ions. It is of course possible that there is an increase in the dielectric constant with the increasing concentration of the electrolyte as is to be expected from the theory of Debye and Hückel. Further, as the adsorption of the chlorine ions is determined by chemical affinity it will be less susceptible to the electrical forces discussed above than will be the case with potassium ions whose adsorption on the above theory is only determined by these electrical forces. We thus see that it is possible to account for the complex manner of variations of the cataphoretic speed on the above basis assuming that the cataphoretic speed is a measure of the surface density and that simultaneous entrainment of the ions of opposite sign is necessary at the time of contact for stable aggregation. A connected picture, however vague of the process of coagulation, adsorption of ions and the electric charge, can thus be presented.

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Some New Reactions of Fusible and Infusible White Precipitates of Mercury and Their Constitution.

By Priyadaranjan Rây and Pareschandra Banerji.

In spite of numerous investigations, the constitution of fusible and infusible white precipitates of mercury was not very clear for a long time till Franklin (*J. Amer. Chem. Soc.*, 1905, **27**, 820; 1907, **29**, 35), from a study of reactions in liquid ammonia and of soda-amide on mercuric chloride, produced strong evidences in support of Hofmann and Marburg's view (*Annalen*, 1899, **305**, 191; *Zeit. anorg. Chem.*, 1905, **46**, 25). Franklin's view about the constitution of these compounds has thus been generally accepted. According to this the infusible white precipitate is regarded as an ammonolysed or ammonobasic compound $H_2N-HgCl$ and the fusible white precipitate as a molecular compound containing ammonia of crystallisation being represented by $HgCl_2.2NH_3$. A large number of facts argue in favour of this view. These have already been discussed by Hofmann and Franklin and need not be detailed here. With a view to further test the validity of this theory we studied the reactions of these bodies with certain reactive substances which were likely to throw some light on their constitution. The results obtained are discussed in the present paper.

Action of Ammoniacal Hydrogen Peroxide upon Infusible and Fusible White Precipitates.

Ammoniacal hydrogen peroxide was found to readily reduce the infusible white precipitate to metallic mercury. The filtrate, after the reaction with hydrogen peroxide, was free from mercury, but contained a large amount of ammonium chloride. An intermediate yellow product was obtained before the reduction to mercury commenced; this was believed to be chloride of Millon's base admixed with mercuric oxide and it gave metallic mercury on ignition.

Fusible white precipitate behaved towards hydrogen peroxide in a similar manner, but the reaction was somewhat slower.

Mercuric oxide also behaves in an exactly analogous way towards ammoniacal hydrogen peroxide.

These reactions are best explained if we assume that the same reduction reaction is involved in all these cases; that is, it is the mercuric oxide on which alone the hydrogen peroxide acts. It is well-known that the hydrolysis of infusible white precipitate follows according to the following equation:

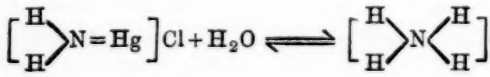
$$2NH_2.HgCl + H_2O \rightleftharpoons NHg_2Cl.H_2O + NH_4Cl.$$

Further hydrolysis leads to the formation of mercuric oxide.

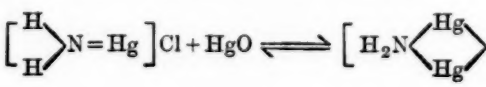
$$NHg_2Cl.\ H_2O + H_2O \rightleftharpoons NH_4Cl + 2HgO.$$

The ammoniacal hydrogen peroxide then acts upon the mercuric oxide reducing it to metallic mercury. The equilibrium is thus disturbed and the whole of the substance is ultimately reduced.

The formation of the ultimate products, mercuric oxide and ammonium chloride by the hydrolysis of the infusible white precipitate argues strongly in favour of its constitution as a substituted ammonium chloride—its hydrolysis being then easily explained as follows:—



The formation of the intermediate product, the chloride of Million's base may be regarded as due to the action of mercuric oxide upon the infusible white precipitate, thus:



Action of Ethyl Mercaptan upon the Infusible and the Fusible White Precipitates.

Perfectly dry infusible white precipitate was treated with an alcoholic solution of ethyl mercaptan under reflux on the water-bath. A small amount of free ammonia was liberated with slight evolution of heat. After some time bright colourless leaflets began to separate when the mixture was cooled and filtered. These were then

fractionally recrystallized and ultimately obtained in three different fractions *a*, *b* and *c*.

Fraction (*a*) forms bright leaflets soluble in hot alcohol with a sharp m.p. at 76°. It was found to contain only Hg, S, C and H and was free from chlorine and nitrogen. It was decomposed by acids wfth formation of diethylsulphide. On dry ignition it gave mercuric sulphide, diethyl sulphide and metallic mercury. (Found: Hg, 61·95. $Hg(SC_2H_5)_2$ requires Hg, 62 per cent.).

$Hg(SC_2H_5)_2$ melts at 76°. So the product is mercury mercaptide.

Fraction (*b*) formed infusible bright leaflets insoluble in water. It was found to contain Hg, S, Cl, C and H and was free from nitrogen. It gave mercuric sulphide, calomel and ethyl sulphide on dry ignition. (Found: Hg, 67·4. $C_2H_5S.HgCl$ requires Hg, 67·5 per cent.). The substance is therefore mercury chloromercaptide.

Fraction (*c*) was highly soluble in water and was found on examination to be pure ammonium chloride.

Fraction (*a*) was obtained in the largest quantity, the yield of the fraction (*b*) being the smallest.

Similar results were obtained when the fusible white precipitate was acted upon by ethyl mercaptan. But in this case the yield of chloromercaptide was fairly large.

The results indicate clearly that the infusible white precipitate can act both as a substituted ammonia and as a substituted ammonium chloride. In the first case the chlorine atom remains attached to the mercury and in the second it is held under the influence of the nitrogen atom. Thus:—

$$H_2N.HgCl \rightleftharpoons [H_2N{=}Hg]Cl.$$

The reaction with ethyl mercaptan then proceeds as follows:—

(*i*) $Cl.Hg-\boxed{NH_2+H}S.C_2H_5 = Cl-Hg-SC_2H_5+NH_3.$

(*ii*) $[H_2N-Hg]Cl+2HS.C_2H_5 = NH_4Cl+Hg(SC_2H_5)_2.$

But as the yield of mercury mercaptide largely preponderates over that of the chloro-mercaptide it may be assumed that in this reaction the infusible white precipitate acts mostly as a substituted ammonium chloride having the constitution $[H_2N{=}Hg]Cl$.

The reaction in the case of the fusible white precipitate can be readily explained by assuming that the latter undergoes partial dissociation as represented below:

$$(i)\ [Hg(NH_3)_2Cl_2] \rightleftharpoons HgCl_2 + 2NH_3.$$

$$(ii)\ [Hg(NH_3)_2Cl_2] \rightleftharpoons [HgNH_2]Cl + NH_4Cl.$$

$HgCl_2$ reacting with the mercaptan gives chloromercaptide and $[Hg.NH_2]Cl$ gives mainly mercury mercaptide with a little chloromercaptide as already explained. Both the above two types of dissociation of the fusible precipitate proceed almost to an equal extent as it gives both mercury mercaptide and mercury chloromercaptide in about equal quantities when treated with ethyl mercaptan.

Action of Thiocarbamide upon Infusible White Precipitate.

When the infusible white precipitate was treated with an alcoholic solution of thiocarbamide, it at once turned black with evolution of a large amount of ammonia. After the reaction was complete, the residue was separated by filtration. The alcoholic filtrate on evaporation left a white crystalline mass. This was dissolved in water and treated with an excess of ammoniacal silver nitrate solution when a yellow precipitate was obtained. The ammoniacal filtrate on being acidified with nitric acid gave a white precipitate of silver chloride only. The white mass left after the evaporation of the alcohol gave ammonia with caustic soda solution. This proved that the alcoholic filtrate contained ammonium chloride. The yellow precipitate obtained by the addition of ammoniacal silver nitrate solution was dissolved in nitric acid, reprecipitated with dilute ammonia, washed and dried. On examination and analysis it was found to be the silver salt of cyanamide. (Found: Ag, 82·4. $CN.NAg_2$ requires Ag, 84·3 per cent.)

The black mass was found to be a mixture of mercuric sulphide and the double compound of mercuric chloride and thiocarbamide.

The same reaction takes place in aqueous solution also. So the action of thiocarbamide upon the infusible white precipitate results in the formation of mercuric sulphide, a double-compound of mercuric chloride and thiocarbamide, cyanamide, ammonia and ammonium chloride.

It is also well-known that mercuric oxide reacts with thiocarbamide forming mercuric sulphide and cyanamide.

As the chlorine of the infusible white precipitate appears partly as ammonium chloride and partly as mercuric chloride in the products of the reaction it may be assumed that it reacts here both as a substituted ammonia and substituted ammonium chloride. In other words it behaves as a mixture of $H_2N.HgCl$ and $[H_2N=Hg]Cl$.

The reaction between thiocarbamide and the fusible white precipitate proceeds almost exactly in the same manner giving rise to the same products.

Action of Thiocarbanilide upon White Precipitates.

An alcoholic solution of thiocarbanilide was found to react readily with the infusible white precipitate without any evolution of ammonia. The products of reaction were black mercuric sulphide, and diphenyl guanidine hydrochloride. The latter was obtained by the evaporation of the alcoholic filtrate. The mechanism of the reaction is best explained by the following equation assuming the infusible white precipitate to be a substituted ammonium chloride.

$$[H_2N=Hg]Cl + SC(NHPh)_2 = Cl[H_2N=C(NHPh)_2] + HgS.$$

(*Cf.* Forster, *Annalen*, 1875, **175**, 35).

The fusible white precipitate reacts in a similar way with an alcoholic solution of thiocarbanilide forming mercuric sulphide, diphenylguanidine hydrochloride and a little ammonium chloride.

As a result of the study of these reactions it may be concluded that the infusible white precipitate can under certain circumstances behave as a substituted ammonium chloride with the chlorine atom directly or indirectly linked to the nitrogen atom. But it is also well-known that the infusible white precipitate generally behaves as a substituted ammonia or as an ammono-basic mercuric chloride as has been established by Hofmann and Franklin. Hence we may now assume that the infusible white precipitate is an equilibrium mixture of these two types of molecules.

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On Induction Period and After-effect in Photochemical Reactions.

By Rukmini Mohan Purakayastha.

It is a well known fact that certain chemical reactions show a well defined period of induction, during which the velocity of the reaction increases up to a maximum. This is then followed by the unusual curve of diminishing velocity characteristic of chemical reactions in general. This period of gradually increasing velocity is known as the period of induction. In some markedly photochemical reactions the same phenomenon has been observed. In dark reactions the induction period may be due to the presence of consecutive reactions, catalysing agents or some sort of passive resistance.

The induction period has already been noted in certain photochemical reactions. The bromination of cinnamic acid and stilbene (Ghosh and Purkayastha, *J. Indian Chem. Soc.*, 1925, **2**, 261; 1927, **4**, 409; 1927, **4**, 553) shows a marked induction period and after-effect. In the oxidation of tartaric acid by bromine an induction period was observed in light by Bunsen and Roscoe (*Pogg. Ann.*, 1857, **100**, 513; *Phil. Trans.*, 1857, **147**, 355, 601) and by Ghosh and Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 165) and in the dark by Sanyal and Dhar (*Z. anorg. Chem.*, 1924, **139**, 161). A mixture of benzaldehyde and acetic acid exposed to the light of an electiric arc also shows the same phenomenon (Jorisen and Ringer, *Chem. Zentr.*, 1905, **76**, 1, 187; *Chem. Weekblad*, **2**, 19). Some reactions were carried out with a view to find out whether the induction period and after-effect are due to the formation of intermediate complex or some other cause.

Experimental.

The Bromination of Cinnamic Acid and Stilbene.

These reactions were investigated with the help of a spectro-photometer and the experimental arrangement was the same as before. It has been already noted (Ghosh and Purkayastha, *loc. cit.*) that after the period of induction and after-effect are over, the reaction

systems on exposure to light again pass through a short period of induction.

The influence of the concentration of the acceptors and also of bromine on the period of induction could not be studied accurately on account of the great reactivity of the substances. The results obtained, however, indicate that as the concentration of bromine increases the period of induction also increases, the velocity of the reaction is, of course, independent of the concentration of bromine. The concentration of the acceptor has no effect on the induction period when the concentration is not very small. The influence of the wave-length of light will be apparent from the previous papers. In blue light where the reactions are very rapid the induction period is quite marked but of a shorter duration while in the yellow the velocity is very small and the induction period is very slight. In carbon disulphide no induction period has been observed in yellow light, but in carbon tetrachloride a slight but rather prolonged period of induction has been observed. The following table will give an idea as to the influence of solvents, the acceptors, the intensity of incident radiation and temperature on the induction period.

TABLE I.

Green light (filters as recommended by Plotnikow).

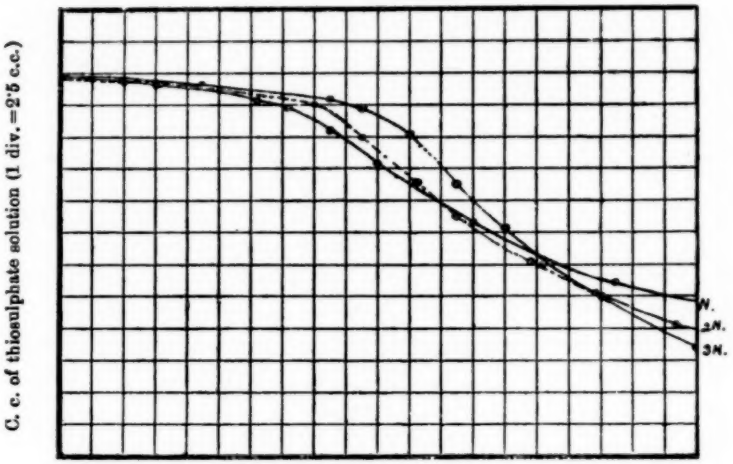
Solvent.	Acceptor.	Conc. of bromine.	Temp.	Intensity.	Induction period in minutes.
CCl_4	Cinnamic acid	·0262M	30°C	1 Hefner	14 to 15
	,,	,,	40°C	,,	5 to 6
	,,	·0197 ,,	30°C	,,	10 to 12
	,,	·0197 ,,	,,	·15	17
	Stilbene	·0197 ,,	,,	1	17 to 18
CS_2	Cinnamic acid	·0197 ,,	,,	·15	7 to 8
	,,	·0197 ,,	,,	1	4 to 5
	,,	·0197 ,,	40°C	·15	3 to 4
	Stilbene	·0197 ,,	30°C	·15	10 to 12

It will be seen from Table I that so far as the effect of these solvents, acceptors, intensity of light and temperature are concerned, anything that increases the velocity causes a diminution in

the period of induction. The velocity of the reaction between stilbene and bromine is less than that of the bromination of cinnamic acid in both the solvents and in all the wave-lengths, but it has a longer period of induction.

Oxidation of Tartaric Acid by Bromine.

This reaction was followed by titration with sodium thiosulphate. The reaction mixtures were placed at the definite distance from a 500 c. p. Pointolite lamp in stoppered bottles. Fig. I shows that



Time in minutes (1 div. = 10 min.)

Fig. I.

the induction period increases with increase in the concentration of tartaric acid. This suggests that the phenomenon may be due to the presence of some sort of impurities or negative catalyst in the acid. Fig. II shows that as the concentration of bromine is gradually increased the induction period increases, reaches a maximum and then again diminishes. An explanation of this behaviour is attempted at a later portion of the paper.

Fig. I gives the results of three experiments in which the concentration of bromine was the same (0·043 N) and the concentration of tartaric acid was N, 2N, and 3N respectively. The influence of the concentration of bromine on the period of induction has been

plotted in Fig. II. The concentration of tartaric acid was 1·55N in all the experiments and the concentration of bromine varied from 0·06N to 0·0092N.

It is evident from the curves in Fig. II that the induction period with 0·0092N bromine solution is 40 minutes which gradually increases to 125 minutes for 0·0306N bromine and again falls to 85 minutes for 0·06N bromine.

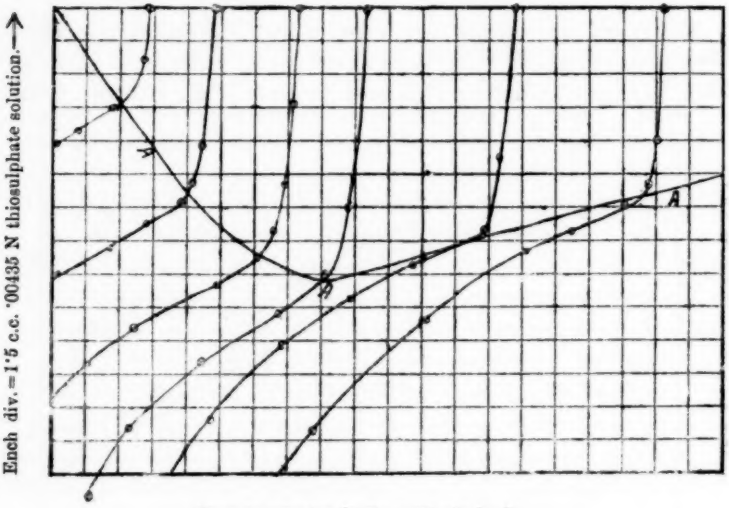


Fig. II.

Oxidation of Mandelic Acid and β-Phenyl-α-Lactic Acid by Bromine.

β-Phenyl-α-lactic acid reacts with bromine in the dark and the reaction is markedly accelerated by light. The reaction between mandelic acid and bromine is a very slow process but it is strongly accelerated by light. The kinetics of both the reactions and their acceleration by light have been studied and will be shortly published. The reaction shows a period of induction when exposed to light and also an after-effect when the source of illumination is withdrawn. The results are given in Tables II and III. The dark reactions are complicated processes. As the rate of disappearance of bromine is strongly influenced by the formation of hydrobromic acid formed in course of the progress of the reactions, the time at which the initial bromine concentration has fallen to the same value in both the light and dark reactions, has been taken for comparison.

TABLE II.

Temperature 25°C. Dark reaction.
Conc. of β-phenyl-α-lactic acid = ·11 N.
Conc. of bromine = ·012 N.

Time in minutes.	Conc. of Br_2 (*In dark*).		K_1 (monomolecular).
0	13·0		—
20	9·9		—
50	7·8		Initial
70	6·8		·00685
100	5·7		·00625
	Exposed to light.		
0	13·5	Induction period.	
4	12·6		
8	10·75		
11	8·95		Initial
	Light cut off.		
31	7·25	After-effect.	·0105
61	5·85		·0085

TABLE III.

Temperature 25°C.
Conc. of mandelic acid = ·125 N. Conc. of bromine = ·01215 N.

Time in minutes.	$(a-x)$.		K_1 (monomolecular).
0	14·3	Period of induction.	—
4	14·15		
8	13·0		
12	10·15		—
15	8·05		Initial.
	Light cut off.		
65	7·5	After-effect.	·000614
125	7·0		·00055

A portion of the same solution was kept in the dark and after about 10 hours the titre of the same volume of solution was found to be 7·65 c.c. of the same thiosulphate solution. The monomolecular constants were calculated by taking this as the zero reading.

Time in minutes.	$(a-x)$.	K_1 unimolecular.
0	7·65	—
60	7·15	·000502
120	6·7	·000480

The after-effect observed in the above case is small. The reaction has also a fairly high temperature coefficient and slight temperature differences may also account for the small after-effect.

The Influence of Potassium Bromide on Induction Period.

It has been found that if potassium bromide is added to the reaction mixtures before exposure to light the induction period completely disappears or considerably reduced. Of course the bromide concentration should be 8 to 10 times greater than that of bromine. If the bromide concentration is small the induction period is observed but it is considerably less. Even in darkness potassium bromide diminishes the induction period appreciably. The results are given in Tables IV, V, VI, VII and VIII.

TABLE IV.

Conc. of tartaric acid = ·375 N.
Conc. of bromine = ·0318 N.
Temperature 55°C. Dark reaction.

Time in minutes.	$(a-x)$.	K_1 (monomolecular).
0	34·0	Induction period.
85	27·1	
110	14·3	—
130	9·0	0·105
141	6·85	·0103
150	5·40	·0106
160	4·0	·0110

TABLE V.

Conc. of tartaric acid = ·375 N.
Conc. of bromine = ·016 N. Conc. of KBr = ·096 N.
Temp. 55°C. Dark reaction.

Time in minutes.	$(a-x)$.	K (monomolecular).
0	17·8	—
35	16·15	·00121
60	14·91	·00129
85	14·0	·00128
115	12·7	·00127
156	11·15	·00130
190	10·0	·00132
240	8·5	·00134

TABLE VI.

Conc. of tartaric Acid = ·23 M.
Conc. of KBr = ·048 M.
Conc. of Br_2 = ·0115 M.
Blue light. Temperature 30°.

Time in minutes.	0	25	70	108	145	190
$(a-x)$	14·4	13·6	12·05	10·7	9·25	7·8
x/t	—	·0320	·0336	·0342	·0355	·0347

TABLE VII.

Conc. of mandelic acid = ·308 M.
Conc. of KBr = ·096 M.
Conc. of Br_2 = ·0175 M.
Temp. 30°. Blue light.

Time in minutes.	0	15	30	50	65	85	105	125
$(a-x)$	22·6	20·75	11·7	16·5	14·5	12·05	9·8	7·35
k/t	—	·123	·130	·122	·125	·124	·122	·121

TABLE VIII.

Conc. of mandelic acid = ·308 M. Temp. 30°C.
Conc. of bromine = ·023 M. Blue light.

Time in minutes.	$(a-x)$,	K_1
0	30·2	Induction period.
10	28·0	
25	25·1	
38	20·4	
45	16·1	·0135
52	13·0	·0140
59	10·6	·0135
71	7·4	·0133

The experimental facts may be summarised as follows :—

(1) Oxidation of tartaric acid by bromine shows a quite marked induction period both in darkness and also in light.

(2) Oxidation of mandelic acid and β-phenyl-α-lactic acid by bromine shows absolutely no induction period in darkness but it is only manifested on exposure to light.

(3) Potassium bromide diminishes and in some cases causes the complete disappearance of induction period.

(4) Bromination of cinnamic acid and stilbene shows an induction period both in light as also in darkness.

(5) In all cases increase of temperature and the intensity and frequency of incident radiation diminishes the induction period.

Ghosh and Basu (this *Journal*, 1928, **5**, 361) has put forward a suggestion to explain the induction period observed in the oxidation of tartaric acid by bromine. They suggest that in the initial stage of the reaction the active bromine atoms are used up in destroying a class of substances known as photo-inhibitors which are almost invariably present in reaction systems and consequently the reaction will proceed at a slower rate in the beginning. On this view it is quite easy to understand the influence of the intensity and frequency of incident radiation. The experimental facts, however, show that this view cannot explain the period of gradually increasing velocity observed in a number of oxidation reactions by bromine.

The existence of the period of induction only in light go to show that in dilute aqueous solutions of bromine probably it is in a hydrated state. It is well known that absorption of moist bromine vapour begins at 6100Å and for bromine solution it begins somewhat earlier. So it is quite reasonable to assume that in aqueous solution bromine molecules will be mostly in the hydrated state. These hydrated molecules are quite reactive in the dark. The reactivity of free bromine molecules is of course greater. When bromine solution is exposed to light free bromine molecules are produced and probably they are then activated. It is obvious that this will require some time and hence there will be a period of gradually increasing velocity and reaction which proceed quite smoothly in the dark will show this phenomenon when exposed to light. This view may also partly account for the large number of molecules found to be transformed per quantum of energy absorbed in these oxidation reactions.

It has been also found that a dilute solution of alcohol (2 or 3%) and bromine shows a period of gradually increasing velocity when exposed to light. These facts suggest that oxidation reactions by bromine will generally show a period of gradually increasing velocity provided the dark reaction is not very rapid and it is fairly strongly accelerated by light.

In presence of a bromide solution of moderate strength only a small portion of the bromine molecules remains in the hydrated state owing to the reaction $Br' + Br_2 \rightleftharpoons Br_3$ and when the concentration of bromide is large in comparison with that of bromine the ratio Br_2/Br_3' may be regarded as constant. The equilibrium constant of the bromide-bromine reaction is ·065 (Jakowkin, *Z. physikal Chem.*, 1896, **20**, 19). It is easy to see that in a ·02 M bromine solution in presence of 2N bromide solution about 65% of bromine molecules will be as Br_3' and in 0·1N bromide the percentage of Br_3' will be about 55. The extinction co-efficient of Br_3' is much greater than that of Br_2 in blue and violet light and there is enough experimental evidence that the activated Br_3' ions do not directly take part in the reaction (results of the author to be communicated shortly). Consequently at such high concentration of Br_3' which has a much greater extinction co-efficient the influence of the hydrated bromine molecules will not be noticeable and the reactions may proceed normally.

At elevated temperatures the induction period considerably diminishes even in absence of any bromide on account of the instability

of the hydrated bromine molecules. On this view the influence of temperature, the intensity and frequency of incident radiation is easily intelligible.

It has been shown that the bromination of cinnamic acid and stilbene and the oxidation of tartaric acid, mandelic acid, and β-phenyl-α-lactic acid shows an after-effect and also a period of gradually increasing velocity. The reaction between hydrogen and chlorine (Taylor's "Physical Chemistry" Vol. II, p. 1220) as has been clearly shown by Weigert and Kellermann shows an after-effect and also an induction period of short duration. No single explanation can possibly account for the existence of the period of induction in all these reactions. The fact that most of the reactions which show an induction period also persist when the source of illumination is withdrawn may lead to the conclusion that the induction period is due to intermediate complex formation.

In the oxidation of tartaric acid by bromine, inhibitors as well as the hydrated state of the bromine molecules are responsible for the existence of this marked induction period and it is more probable that the inhibitors play the more important role. A reference to Fig. II will make it evident that though the concentrations of the bromine solutions are widely different, the reactions proceed normally when practically the same amount of bromine has been used up in all the reaction mixtures. This clearly shows that two side reactions are taking place, namely the normal reaction between bromine and tartaric acid and also the removal of the inhibitor by bromine. The reaction proceeds normally from the instant at which all the inhibitor has been completely oxidised. In the oxidation of mandelic acid and β-phenyl-α-lactic acid, which show no induction period in darkness, the hydrated state of the bromine molecules is alone responsible for the existence of the period of gradually increasing velocity. In hydrogen-chlorine reaction the cause is probably associated with the presence of photo-inhibitors. In the bromination of stilbene and cinnamic acid the induction period is mainly due to the formation of intermediate complexes. The reappearance of the short period of gradually increasing velocity strongly supports this view. The induction period, however, depends also to some extent on the association of bromine molecules with the solvents, and the explanation will be similar to what has been suggested in the case of the oxidation reactions. Extinction coefficient measurements of bromine in different solvents give widely

different values (Plotnikow, *Z. physikal. Chem.*, 1912, **79**, 357), Ghosh and Purkayastha, this *Journal*, 1927, **4**, 409) and the natural conclusion is that the bromine molecules are associated with the different solvents.

An explanation may be here put forward for the induction period (Fig. II) observed with bromine solutions of different concentrations in the oxidation of tartaric acid. It has been already noted that in the bromination reactions the induction period increases with increase in the concentration of bromine. So the lower portion of the Curve A in Fig. II is of the same nature. The solubility of bromine in organic solvents is enormously greater than its solubility in water. Even in dilute aqueous solutions, after a certain concentration is reached, there will be appreciable quantities of free bromine molecules and if the concentration is increased beyond this the proportion of free bromine will increase more rapidly and a considerable portion of the reaction will be due to the free bromine molecules. Hence on increasing the bromine concentration beyond this stage the induction period will gradually diminish because of the presence of more and more bromine molecules which have a much greater reactivity.

A fairly large number of reactions is however known which show only an after-effect. The mechanism of the after-effect has not yet been explained. Dhar and Mukherjee (this *Journal*, 1925, **2**, 277) investigated a number of reactions exhibiting after-effect and put forward the view that the after-effect might be due to the activation of the inactive molecules by the impact of the activated molecules of the reacting substances. This process will require sometime to die out even after the source of illumination is withdrawn. It should be pointed out here that on proper calculation it will be found that some of the reaction studied by Dhar and Mukherjee do not show any after-effect at all. Calculation of molecular constants should have been made from the instant when the source of illumination is cut off.

It seems more probable that the after-effect is due to the existence of chain reactions and Weigert's suggestion (*Ann. Physik*, 1907, **24**, 243) that intermediate complexes or intra-molecular transformation of the light absorbing substances may serve as reaction nuclei in photo-chemical changes is in line with this view. Dhar and Mukherjee think that there is absolutely no experimental fact in favour of intermediate complex formation. It may be said

however, that though there is no direct evidence, some facts indirectly point to the above conclusion. It has been found that in reactions of this type a large number of molecules are transformed per quantum of energy absorbed and consequently the existence of chain reactions or intermediate complex formation may be regarded to be the more probable view.

In conclusion my best thanks are due to Prof. J. C. Ghosh for his suggestions and encouragement.

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Tetraethylphosphonium Nitrite.

By Prafulla Chandra Rây and Nirmalendunath Ray.

One of us has described the preparation of ammonium nitrite (Rây, *J. Chem. Soc.*, 1909, **95**, 345) and also that of alkyl ammonium nitrites (Rây and Rakshit, *ibid*, 1911, **99**, 1017, 1470). In continuation of this work the preparation of tetraethylphosphonium nitrite has been undertaken.

Method of Preparation.—Tetraethylphosphonium iodide* and pure recrystallised silver nitrite were triturated in a mortar in presence of minimum quantity of water, care being taken that in the filtrate there was a slight excess of silver nitrite. The latter was removed by cautious addition of a dilute solution of tetraethylphosphonium iodide until neither of the reacting substances was in excess. It was however found that a considerable quantity of tetraethylphosphonium iodide was lost as it forms an insoluble double salt with silver iodide (*cf.* Masson and Kirkland, *J. Chem.*

* As considerable quantities of tetraethylphosphonium iodide were required for our present purpose as also for the preparation of tetraethylphosphonium sulphate—a component of a series of double salts with the sulphates of the copper-iron group, a detailed account of the preparation of the parent substance is given below :—

Hofmann's method was naturally tried first (*Annalen*, 1857, **104**, 16). Frequent explosions, however, took place during heating phosphonium iodide with ethyl alchhol in a sealed tube. This method was, therefore, abandoned in favour of that of Masson and Kirkland (*J. Chem. Soc.*, 1889, **55**, 138). These chemists had to use a large quantity of silver oxide in view of the fact that a considerable amount of hydriodic acid is formed after reduction of the polyiodides with sluphuretted hydrogen and also that unless an excess of moist silver oxide is used a portion of the tetraethylphosphonium iodide is likely to be lost in the form of an insoluble double halide with silver iodide. They, however, suggest the alternative process in which the aqueous solution of the tetraethylphosphonium iodide containing a large quantity of hydriodic acid is treated with potassium carbonate when the tetraethylphosphonium iodide separates out as an oily layer on the top. The 'oil' is then partly evaporated on the water-bath when crystals begin to appear. It is dried in a desiccator and is then taken up with alcohol and finally precipitated with ether. The product, however, was found to be contaminated with potassium iodide, a fact which seems to have been overlooked by Masson and Kirkland. It had, therefore, to be redissolved in water and again separated from the solution by the addition of potassium carbonate as above. It was often necessary to repeat the process twice or thrice in order to remove the last traces of potassium iodide. The yield however is greatly reduced.

Soc., 1889, **55**, 136), a product of the reaction. As the yield of the nitrite was consequently too low, an alternative method was adopted. The tetraethylphosphonium iodide was treated with an excess of silver oxide. The hydroxide thus obtained was neutralised with dilute sulphuric acid. The sulphate of the base was then treated with the requisite amount of pure recrystallised barium nitrite. The tetraethylphosphonium nitrite obtained in solution was filtered and evaporated in a vacuum over sulphuric acid.

Properties.—Tetraethylphosphonium nitrite is a crystalline compound, having a faint yellowish tint, characteristic of the nitrites in general. It is very deliquescent and therefore great care had to be exercised in handling the substance in the atmosphere of the laboratory.

Analysis:—

Found: N, 7·07; P, 16·34; C, 48·25; H, 10·64.

$(C_2H_5)_4PNO_2$ requires N, 7·25; P, 16·06; C, 49·74; H, 10·44 per cent.

N.B.—Owing to the extremely deliquescent character of the nitrite it has been found very difficult to keep it from absorbing moisture from the atmosphere at the time of weighing and this probably accounts for slightly low results in the estimation of nitrogen.

The phosphorus was estimated by heating the substance in a sealed tube with nitric acid (*d* 1·5) as in Carius' method for four hours. After opening the tube, the excess of nitric acid was evaporated nearly to dryness and the acid neutralised with sodium carbonate. The mass was then transferred to a platinum crucible and fused with potassium nitrate and sodium carbonate. The filtrate was acidified with hydrochloric acid and the phosphorus precipitated with magnesia mixture. It was found that the phosphorus often came out too low. This evidently was due to the fact that a portion of the alkylphosphine escapes oxidation.

The carbon also sometimes comes out even lower. Traces of alkylphosphine, it would appear escape, oxidation, however longer the column of oxide of copper be interposed during combustion and however cautiously the heating be effected.

The physical properties of the tetraethylphosphonium nitrite will form the subject of a subsequent communication.

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Variation of the Electrical Charge of Colloidal Particles. Part IV. The Effect of Dilution on the Charge of Colloidal Particles in the Presence and Absence of Electrolytes.

By Jnanendra Nath Mukherjee, Satya Prasad Rai-Chaudhuri and Ardhendu Sekhar Bhattacharyya.

The work of Mukherjee, Chaudhury and Rai-Chaudhuri (*J. Indian Chem. Soc.*, 1927, **4**, 493) on the variation of the charges of arsenious sulphide sols on dilution has been continued in the present paper which also records some interesting observations on ferric hydroxide sol. The conditions for obtaining accurate values for the cataphoretic speed of the particles of ferric hydroxide sol have not been carefully investigated. The question of what constitutes a suitable upper liquid for a particular sol is a problem which must be solved for each sol in a manner indicated in previous papers (*Proc. Roy. Soc.*, 1923, **103A**, 102 ; also *J. Indian Chem. Soc.*, *loc. cit.*). It seems that simpler modifications of the above method (*cp.* Freundlich and Zeh, *Zeit. physikal. Chem.*, 1925, **114**, 84 ; Kruyt and Willigen, *Zeit. physikal. Chem.*, 1927, **130**, 170 ; and *Koll. Zeit.*, 1928, **44**, 22) are not always satisfactory and they should be used after the boundary conditions have been fully investigated.

Discussions as to the conditions of coagulation are always based on certain assumptions as to the electric charge. There are very few observations on these points. The meagre data that are available for or against such assumptions have mostly been obtained by the use of the arrangement of Burton ((*Phil. Mag.*, 1906, vi, **11**, 425) or its modifications and they are not reliable as the conditions obtaining at the boundary were not investigated.

Experimental.

Mukherjee's cataphoretic method has been used (*loc. cit.*) in this investigation. Two different U-tubes were used, of which

the one having three side tubes and an effective distance of 3·1 cm. between the side tubes enclosing the boundary for both the upward and downward movements was used for the work with the ferric hydroxide sol and the other had two tubes and an effective distance of 4·2 cm. for both movements and was used for all other measurements. Viscosity corrections have been made and rates of migration have been given in centimeters per second per volt/second multiplied 10^5 times. The temperature of the thermostat was $35° \pm 0·1°$. In the case of the higher concentrations of the electrolyte the heating effect, on account of the greater conductivity, was tested by placing a milli-ammeter in the circuit of the cataphoretic tube and also by inserting a narrow clinical thermometer inside one of the limbs while the potential between the electrodes was maintained constant. The increase in the current strength on its continued passage for over half an hour could not be detected. The rise in the temperature indicated by the clinical thermometer after half an hour was about 2°F. The consequent change in viscosity is not likely to be more than 2—3%. The boundary remained sharp and flat up to the highest concentrations.

(1) *Ferric Hydroxide Sol.*

Preparation.—Ten c. c. of a saturated solution of ferric chloride were added to 500 c. c. of boiling conductivity water drop by drop with constant stirring and the mixture was then boiled for about 20 minutes. The sol was then cooled and allowed to be dialysed (for about a month and a half) till no trace of iron could be detected in the outer liquid. The dialysis was continued till only a faint trace of chlorine could be detected. It was then stored in clean wide-mouthed Jena glass bottles. In previous measurements of the cataphoretic speed of this sol equiconducting solutions of electrolytes, *e. g.*, potassium chloride (*cp.* Burton, *loc. cit.*) have been used as the upper liquid assuming that this procedure secures a constant potential gradient during the movement. It will be found from what follows that unless the upper liquid procures *the same ionic environment*, as exists in the colloid, the measurements are definitely in error. The ultimate procedure which gave a constant potential gradient and an identical rate for the original sol both for direct and reverse movements was as follows : The sol was coagulated with a few drops of a concentrated solution of K_2SO_4

and the p_H of the supernatant liquid after coagulation was determined colorimetrically. A solution of hydrochloric acid having the same p_H was made equally conducting with the sol by adding to about 500 c. c. of this solution the requisite quantity (a few drops) of the saturated ferric chloride solution, used in the preparation of the sol so that the volume of the dilute hydrochloric acid solution did not change materially. This solution was found satisfactory as the upper liquid. It has been however found that a hydrochloric acid solution having slightly higher p_H is more satisfactory probably because of the fact that on the addition of the small volume of concentrated ferric chloride solution the p_H becomes lower. The results are given below. The p_H values given in Tables I—III refer to the supernatant liquid after coagulation as described above.

TABLE I.

Pure Sol A ; p_H 3·2 ; 0·042 moles of Fe_2O_3 per litre.

Upper liquid.	Upward.			Downward.		
	Potential gradient.		Rate of migration.	Potential gradient.		Rate of migration.
	Before.	After.		Before.	After.	
KCl	0·661	0·647	29·2	0·573	0·900	87·2
LiCl	0·709	0·707	16·8	0·688	0·860	88·0
KCl in ·001N-HCl	0·678	0·694	26·6	0·662	0·878	50·8
HCl	0·552	0·775	46·4	0·767	0·460	44·0

TABLE II.

Pure Sol B; p_H 2·9; 0·0342 moles of Fe_2O_3 per litre.

Upper liquid.	Upward.			Downward.		
	Potential gradient.		Rate of migration.	Potential gradient.		Rate of migration.
	Before.	After.		Before.	After.	
HCl	0·647	0·817	56·5	0·796	0·682	50·2
LiCl in ·001N-HCl	0·765	0·790	37·7	0·737	0·859	52·8
LiCl	0·590	0·586	32·5	0·586	0·776	63·6
$FeCl_3$ in ·001N-HCl	0·707	0·764	44·2	0·773	0·704	47·4
$FeCl_3$ in ·00067N-HCl	0·671	0·671	53·4	0·675	0·673	49·5

TABLE III.

Sol B at different dilutions.

Dilution. Volume of sol : Volume of water.	Resistance in ohms in the same cell.	PH of upper liquid after coag.	Upward. Potential gradient. Before.	Upward. Potential gradient. After.	Upward. Rate of migration.	Downward. Potential gradient. Before.	Downward. Potential gradient. After.	Downward. Rate of migration.	Depression of boundary in 20 min.
Sol B	192	2·9	0·671	0·671	53·4	0·675	0·673	49·5	Nil
1:1	542	3·7	0·688	0·688	54·5	0·698	0·688	51·7	Nil
1:3	932	4·5	0·694	0·708	52·9	0·708	0·677	57·4	Nil
1:5	1304	4·7	0·679	0·676	54·1	0·676	0·672	72·1	·29 cm. taken before expt.
1:10	2540	5·4	0·771	0·773	46·4	0·777	0·773	81·7	·15 cm. taken after expt.
1:20	3250	5·6	0·758	0·780	48·7	0·786	0·767	80·7	·28 cm. in 10 min. before expt.

TABLE IV (Fig. I).

Dilution.	B	B/2	B/3	B/5	B/10	B/20
Mean rate of migration.	51·5	53·1	55·1	63·1	64·1	64·7

It will be seen from Tables I and II that the potential gradient does not at all remain constant during cataphoresis in both directions except when the mixture of ferric chloride and hydrochloric acid prepared as stated above is used as the upper liquid. The other electrolytes also show a great difference in the values of the direct and reverse movements. Hydrochloric acid alone secures a steadier potential gradient but the difference between the movements in opposite directions is still marked. That this difference does not result from the speed or free fall of the particles would be apparent from column X, Table III. The constancy in the cataphoretic speed when the rate of free fall is negligible and of the potential gradient for movements in both directions indicates that the particles are moving in a '*uniform ionic environment*' (*cp.* a paper by one of us on the theory of cataphoretic measurements to be published in the Journal of the Indian Chemical Society).

We find from Table II that the rate of downward movement of the sol at higher dilutions is considerably greater than that of the upward movement even when the condition of steady potential gradient has been attained and that the particles have a rate of settling comparable to the cataphoretic speed. It appears that the rate of settling on account of gravity during cataphoresis is difficult to measure. Different values are obtained according as the rate is measured after the boundary rises to the level necessary for the measurement and before the cataphoresis begins or after the cataphoresis has stopped. Similar observations have been previously recorded with gold sols in Part II of this series. The value given in the last column in Table III, however, shows that the rate of free fall is considerable and is observable only at higher dilution beginning from 1:5. The mean of the two movements in the up and down directions should give the correct cataphoretic speed as the rates of settling vary in the same manner for both movements. The mean cataphoretic speeds given in Table IV show this as we get a constant speed after a certain dilution. Table IV shows that the cataphoretic speed increases on dilution and becomes constant at higher dilutions. The sols A and B have a fairly high concentration of free acid and it is probable that the amount of ferric ions adsorbed by the particles does not alter to any marked extent on dilution. This can be expected if we remember that the reaction between ferric hydroxide molecules on the surface and hydrogen ion is chemical. On diluting the sol the chlorine ion concentration decreases which thereby decreases the electrical adsorption of chlorine ions on the surface so that the density of the charge increases. It is difficult to reconcile the observed increase in cataphoretic speed with the lower coagulating concentration of ferric hydroxide sol on dilution which has been previously observed by several authors. This question will form the subject matter of a separate paper.

On keeping the U-tube filled with the colloid and a pure solution of lithium chloride as upper liquid overnight it was found that the upper liquid becomes faintly yellowish brown but this liquid did not show any marked Tyndall effect when examined by light from an ordinary lamp. This observation shows that the colloid contains a trace of free ferric ions which diffuse into the upper layer. On the other hand the uper liquid prepared by mixing hydrochloric acid and ferric chloride as described above, though it appears colourless to the naked eye when freshly prepared (it also remains colourless during

the measurement), becomes coloured on keeping overnight. It is likely that the concentration of free ferric ions in the colloid is lower than that in the upper liquid we have used.

The observations made above lead to the conclusion that there are some free H^+ions and Cl^-ions in the sol itself possibly also some free Fe^{+++}ions in addition to the charged colloidal particles. For any precise statement however we must know the accurate composition of the sol itself and await further investigation.

(2) *Arsenious Sulphide Sol.*

A saturated solution of arsenious oxide was mixed with twice its volume of conductivity water. One litre of the diluted solution was added to a litre of conductivity water saturated with hydrogen sulphide, a thin stream of which was continued till a trace of arsenious acid was left free in the solution (*cp.* Mukherjee and Choudhury, *J. Indian Chem. Soc.*, 1925, **2**, 296). The sol contained about 16 milli-moles of arsenious trisulphide per litre.

For upper liquid in this sol an equally conducting hydrochloric acid solution was used (*cp.* Mukherjee, *loc. cit.*)

TABLE V.

Arsenious Sulphide Sol A.

Dilution. Volume of pure sol : Volume of water.	Rate of migration.		
	Direct.	Reverse	Mean (corrected for viscosity).
Pure	72·9	70·6	74·1
1:1	67·4	65·0	65·8
1:5	62·3	55·4	58·3
1:10	49·2	45·5	46·3

TABLE VI.

Sol A diluted 1:1.

Conc. of potassium chloride in normality.	Rate of migration.		
	Direct.	Reverse.	Mean.
0	67·4	65·0	65·8
0·001	55·1	54·38	54·7
0·01	54·7	32·5	53·6
0·05	65·5	59·6	62·6
0·056	66·7	65·9	66·3
0·056*	67·8	69·7	68·8

TABLE VII.

Sol A diluted 1: 5

Conc. of potassium chloride in normality.	Rate of migration.		
	Direct.	Reverse.	Mean.
0	62·3	55·4	58·4
0·001	49·8	46·3	48·1
0·01	51·5	50 1	50·8
0·05	58·6	57·9	58·3
0·067	60·3	62·6	61·5
0·067*	50·6	50·5	50·6

* After coagulation.

TABLE VIII.

Sol A diluted 1 : 10.

Conc. of potassium chloride in normality.	Rate of migration.		
	Direct.	Reverse.	Mean.
0	49·2	45·5	46·3
0·001	50·3	45·0	48·2
0·01	53·0	52·7	52·9
0·05	64·7	59·2	61·9
0·067	75·2	69·8	72·5
0·071	67·7	66·6	67·2
0·077	68·1†	47·3*	—

The results for zero concentration of electrolyte in Table IV are shown graphically in Fig. I. The variations of charge with different

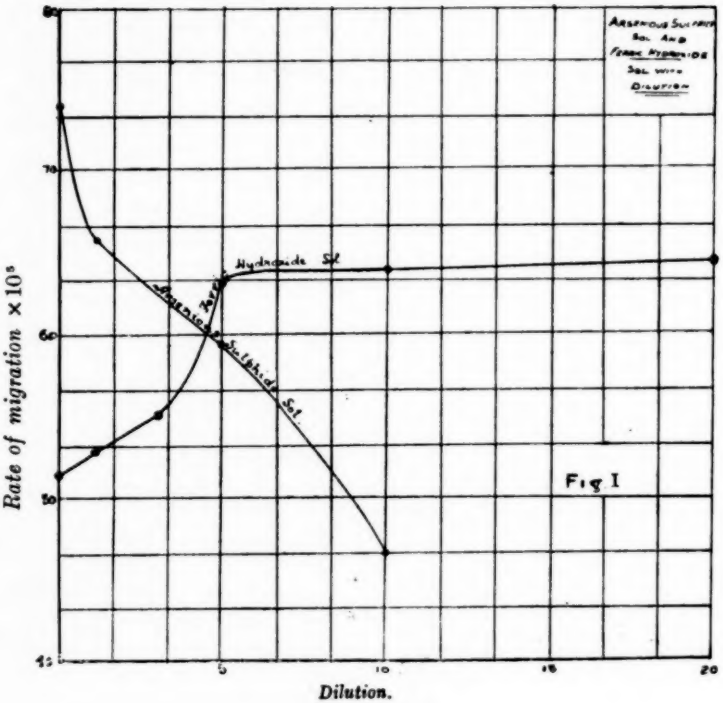
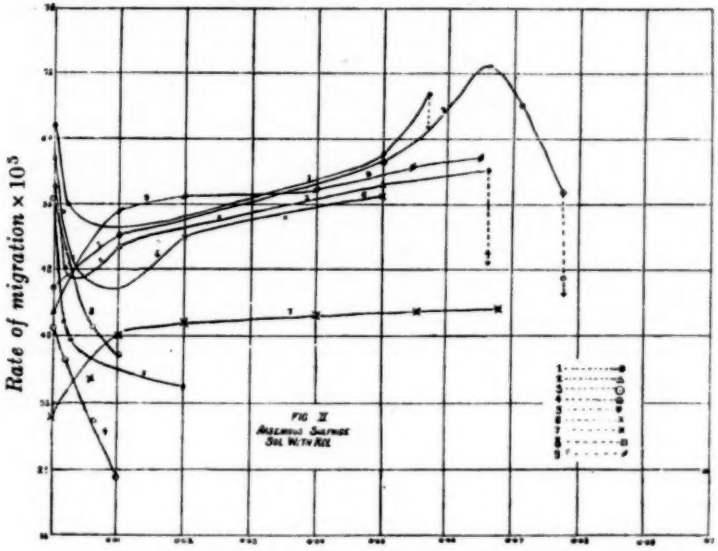


FIG. I.

† The sol coagulated during the measurement.

* After coagulation.

concentrations of potassium chloride at different dilutions of sol as given in Tables VI, VII and VIII are plotted graphically in Fig. II in Curves 1, 2, 3 respectively.



Concentration of electrolyte in normality

FIG. II.

DISCUSSION.

(a) *General.*

The only reliable measurements of the cataphoretic speed of colloidal arsenious sulphide particles in presence of potassium chloride apart from those published from this laboratory are those of Freundlich and Zeh (*loc. cit.*) who took cognisance of the improvements suggested by Mukherjee (*loc. cit.*). They observed a gradual decrease in the cataphoretic speed with increase in concentration up to a concentration of ·01N (*loc. cit.*, p. 84). They, however, consider their measurement at concentrations higher than ·002N to be uncertain (*vide* foot-note, p. 84). Their values are given in Curve 4, Fig. II. Curve 5 has been plotted from the data of Mukherjee, Chaudhury and Rai-Chaudhuri (*loc. cit.*). Mr. S. G. Chaudhury in this laboratory observed in 1925 that with a particular sample of arsenious sulphide sol potassium chloride showed a peculiar behaviour of a decrease in charge at low concentrations followed by a rise at

higher concentrations. But lithium chloride and hydrochloric acid did not show this peculiarity up to the concentration studied (·005N and ·01N respectively). It was thought desirable to confirm this observation fully before publication. His data are now given in Curve 6, Fig. II. Since then Kruyt and Willigen (*loc. cit.*) have recorded a continuous increase in the charge with increasing concentrations of potassium chloride as shown in Curve 7, Fig. II. It is obvious that the run of the curves depends on the quality of the sol. The measurements of Freundlich and Zeh (*loc. cit.*) were not made at 35°. They took measurements at 20°. The temperature at which Kruyt and Willigen worked is however not given in their paper.* From Freundlich and Zeh's figure one can calculate the values of the cataphoretic speed at 35° assuming that the mobility varies inversely as the viscosity of water. It is not claimed that these corrected values represent the actual values at that temperature and they are given in Curve 8 only for the sake of comparison. In Part II of this series of papers a slight initial decrease followed by a rise was observed with sodium citrate and potassium ferrocyanide. These observations show that the influence of an electrolyte on the cataphoretic speed is much more complex than has hitherto been supposed to be the case and that the quality of the sol determines this behaviour. As to the actual factors which are responsible for this difference, it is not possible to say anything definite pending further investigations. The theoretical considerations set forth by one of us (*Trans. Far. Soc.*, 1921, **16**, 103 ; *Phil. Mag.*, 1922, **44**, 321 ; *J. Indian Chem. Soc.*, 1925, **2**, 191) and the experimental work in this laboratory enable us to give a plausible physical picture. Before proceeding to consider this tentative explanation, it is necessary to discuss two aspects of Curves 1—3.

(*a*) *Cataphoretic Speed and Coagulating Concentration.*

Kruyt and Willigen (*loc. cit.*) found no diminution in the rate of migration up to the highest concentration (·066N) they used but their observations did not extend to the coagulating concentration (·08N). They assume that at the coagulating concentration the

* In a later paper they mention that their measurements were taken at 20°. Curve 9 has been plotted from their data after correcting for the lower viscosity at 35°.

cataphoretic speed is much greater than that of the pure sol and attempts to explain it on the ground that the dielectric constant of the medium increases at these high electrolytic concentrations to such an extent that the potential of the double layer is really smaller in spite of the increase in cataphoretic speed. They conclude that coagulation takes place at a critical potential as postulated by Powis and state, "Diese Kataphoretischen Messungen widersprechen deshalb nicht notwendig Powis'sche Theorie des kritischen Potentials (p. 176)." Excepting the measurement of Powis (*Zeit. physikal. Chem.*, 1915, **89**, 186) by Burton's method (*loc.cit.*) which certainly gives erroneous results in the case of arsenious sulphide sols, there are no measurements of cataphoretic speed extending to the coagulating concentration. In Curves 1, 2, and 3 we have the first reliable evidence that coagulation actually takes place at a much higher cataphoretic speed than that for the "pure" sol. It may also be remarked that we do not measure the potential directly but we calculate it from the cataphoretic speed. Working on arsenious sulphide sols Rai-Choudhuri and others (*loc. cit.*) have shown that with some electrolytes coagulation does not occur even when the cataphoretic speed is as low as 9, though with some other electrolytes coagulation occurs at a cataphoretic speed of about 43. They pointed out that "the stability is not so directly related to the charge as is generally believed to be the case. Thus the electrolytes with divalent cations depress the charge enormously. We have stable sols with these electrolytes where the particles show a rate of migration ranging from 20 to as low as 9 (calcium benzoate). From the slope of the curve with potassium, sodium or lithium chloride as the added electrolyte, it would appear that coagulation takes place before a velocity of about 20 has been reached. We would particularly refer to the low charge with calcium benzoate (pp. 513-14)." It has also been observed (*J. Indian Chem. Soc.*, 1925, **2**, 296) that at the same hydrogen ion concentration the cataphoretic speed is always greater for hydrochloric acid than for acetic acid though the former has an incomparably greater coagulating power. *It is evident therefore that the current belief regarding the existence of a critical potential characteristic of the coagulating concentration of different-electrolytes for a given sample of a colloid is erroneous.*

An explanation of the non-existence of a critical cataphoretic speed has been given by one of us in previous papers (*loc. cit.*, also

previous papers). In these discussions it has been assumed that the cataphoretic speed is a measure of the density of the charge on the surface. This assumption is in conformity with Lamb's equation*:

$$e.H=\overline{\beta}.u \ldots\ldots\ldots\

in the equation of cataphoretic speed unless one assumes that the thickness of the double layer is proportional to the dielectric constant. While such a relationship may appear probable on theoretical grounds * it does not help us in the present discussion, as it has been observed by A. Nagaraja Rao in this laboratory that curves of similar form are obtained if one uses a dilute (up to 10 per cent.) alcoholic solution of potassium chloride. It would thus appear that a much more detailed theoretical treatment than is customary is required, for variations in dielectric constant as suggested by Kruyt cannot account for the shape of Curves 1, 2 and 3. We find from Fig. II that the run of Curve 5, which gives the measurements recorded in our previous paper, agrees with Freundlich's (Curve 4) and that they conform to the usual assumption that coagulation takes place at a lower cataphoretic speed. All the other curves differ in this respect from these two curves. It is therefore interesting to know that the sol used in the previous paper was prepared in the manner usually described in papers from Freundlich's laboratory as follows:—"A saturated solution of arsenious oxide was mixed with twice its volume of conductivity water and the resulting solution was added to an equal volume of the water saturated with hydrogen sulphide which was then passed through the solution until all the arsenic had been transformed into arsenious sulphide. This took about one hour and a half. Then a current of hydrogen was passed till the sol was perfectly free from hydrogen sulphide. The sol was kept in Jena glass bottles wrapped up with black paper in a dark place but as care was not taken to have arsenious acid in excess polythionic ions may be present. The sols contained about 16 millimoles of arsenious trisulphide per litre." (*loc. cit.*, p. 497). Choudhury and Kundu, (*J. Indian Chem. Soc.*, 1926, **3**, 345) have shown that the particles of the sol prepared in this manner have got a chemical composition different from those of the sols used in this investigation in which care has been taken to stop the stream of hydrogen sulphide in time to leave an excess of free arsenious acid. To this difference in chemical composition should be referred the decrease in the cataphoretic speed at high concentration of electrolyte generally observed by Choudhury and others. A comparison of Curves 3 and 9 in Fig. II also shows that they have more or less the same form

* There are other possibilities which will form the subject of a separate communication.

and refer to two sols which have the lowest initial cataphoretic speed. *The increase in dielectric constant at high concentrations is a necessary assumption in order to explain the difficulty that coagulation takes place at a much higher cataphoretic speed. But it does not seem to be a sufficient explanation.* We have also to account for the great difference in the shapes of curves and as the electrolyte and its concentrations are common factors we have also to assume the existence of specific factors. As mentioned already small additions of alcohol bring out more strongly the peculiar shape of these curves.

(*b*) *The Mechanism of Coagulation.*

The most interesting peculiarity of Curves 2 and 3 is the change in speed after coagulation showing that some irreversible change has set in after coagulation (Mukherjee and Mazumdar, (*J. Chem. Soc.*, 1924, **125**, 785). This decrease in the cataphoretic speed is not due to the settling of the coagulum as the direct and reverse movements agree. Here also the effect depends on the quality of the sol. The dilute sols show this effect and the original sol does not show it. The coagulating concentrations of arsenious sulphide sols on dilutions do not show any such complicated behaviour as the cataphoretic speeds in Curves 1, 2 and 3. Mention may be made in this connection that addition of non-electrolytes, or weak or organic acids (Chaudhury and others, *J. Indian Chem. Soc.*, 1926, **3**, 253-55) does not in several instances alter the coagulating concentration in the least. These considerations make it plausible that the nature of the coagulating ion determines to a large extent its coagulating concentration. Probably two particles where they touch each other after performing the electrical work referred to above can form a stable aggregate only when they have simultaneously entrained in the surface of contact on equivalent amount of the oppositely charged ion. Such a condition necessarily limits the percentage of successful collisions and make it dependent on the kinetics of the ionic interchange between the double layer and the bulk of the liquid. The concentration of the coagulating ion, its valency and its mobility will be factors affecting the process. This idea is similar to that of Whetham with this difference that the electric work mentioned above comes in as an additional factor. Where coagulation takes place at low concentration of electrolytes, *e.g.*, those having polyvalent coagulating ions the electrical work is probably the

determining factor. At high concentration of electrolytes it is possible that the facilities for entrainment are the more important.

The Cataphoretic Speed and Adsorption of Ions.

Regarding the variation of the cataphoretic speed with the concentration of the electrolyte we shall proceed on the basis that the cataphoretic speed is proportional to the density of charge on the surface. As stated before Curves 5 and 4 (or 8) refer to sols which contain a greater percentage of sulphur than that indicated by the formula As_2S_3. The surfaces of the colloidal particles of these two sols are probably fully covered by hydrosulphides (these sols smell of hydrogen sulphide on keeping) and the anion adsorption is weak for these sols (compare *J. Chem. Soc.*, 1924, **125**, 794). Consequently we get a continual decrease in cataphoretic speed with increasing concentration of electrolytes (*vide* Curves 4 or 8 and 5). It would be interesting to find what happens at still higher concentrations. The greater effect of divalent cations (*vide infra*) would indicate their greater adsorbability but coagulation takes place at a lower cataphoretic speed on account of the low concentration of the cation and the consequent smaller probability of entrainment of ions.

The sol prepared by the other method contains a smaller proportion of sulphur and an excess of arsenious oxide. It has also a higher charge. We would imagine that the surface of these particles contain a much smaller amount of hydrogen sulphide in a state of adsorption on account of the excess of arsenious oxide and the corresponding smaller concentration of hydrogen sulphide in the bulk of the liquid. For the same reason probably divalent sulphidions instead of hydrosulphidions are present on the surface so that the surface density of the charge is greater. The surface should in that event contain a larger number of places available for the adsorption of anions. So long as the density of the surface charge remains high in view of the divalent nature of the sulphidions and the electrical repulsion against chloridions the adsorption of potassium ions predominates. As the charge decreases the adsorbability of the potassium ion becomes progressively weaker and that of the chloridions greater and ultimately predominates over the former. One would expect that when the surface has been nearly saturated with chloridions the adsorption of the potassium ion would again predominate and a decrease in the charge would be noticeable. There is

evidence for this statement in Curve 3. As dilution proceeds the initial charge diminishes indicating a smaller number of sulphidions and a greater capacity to adsorb chloridions. When the initial charge is sufficiently low as in Curves 3 and 7 (or 9) the adsorption of chloridions predominates from the beginning. Coagulation takes place at higher cataphoretic speed probably as the result of a balance between the opposite effects of the higher dielectric constant pointed out by Kruyt and of the increased facilities for the entrainment of oppositely charged ions. The increase in the dielectric constant if fully established would also explain the fact that coagulation takes place at a higher cataphoretic speed when the coagulating ion is univalent which has been observed with the other type of the sol. The great drop in cataphoretic speed on coagulation may be imagined to result from irreversible aggregation when the particles form common surfaces and the neighbouring molecules suffer a rearrangement passing on to a more regular arrangement in conformity with its crystalline character so that the primarily adsorbed anions and their partner cations are loosened from the surface and a diminution in the density of the charge on the surface takes place. Such a state of affairs appears to be plausible in the light of the observations of Freundlich ("Kapillarchemie," 1922, pp. 622-632; *cp.* specially Freundlich and Schucht, *Z. physikal. Chem.*, 1913, **85**, 660). The following remarks of Freundlich are quoted below:

"Es ist auch, wie Zsigmondy (*Nachr. D. K. Gotting Gesellsch. d. Wissensch.*, 1917, S. 33) mit Recht bemerkt, nicht notwendig, dass die Einzelteilchen in diesen frisch koagulierten Flockem unmittelbar aneinander haften müssten ; sie können sehr wohl noch durch ultramikroskopische Flüssigkeitshaüte getrennt sein. * * * Auch jetzt wird die vorhandene Ladung eine Abstossung bedingen, dieum so grösser ist, je grösser diese Ladung, und nur die Teilchen die bei ihren Schwingungen mit einer gewissen kritischen Wucht zusammenstossen, werden sich unmittelbar beruhren, inniger vereinigen und verschmelzen. Die erforderliche kritische Wucht ist um so kleiner, je geringer die Ladung, je grösser die Koagulatorkonzentration ist voraus-gesetzt, dass noch keine Umladung jenseits des isoelektrischen Punktes stattgefunden hat. Je grösser die Koagulatorkonzentration ist, und je kleiner damit die Ladung, um so grösser also auch die Zahl der Teilchen, die die nötige Wucht haben, um so grösser also auch die Geschwindigkeit des Vergröberns und des Adsorptionsrückganges. * * * * * * * *

Diese Theorie vernachlässigt, vielleicht zu Unrecht, den Umstand, dass die Flocken bei verschiedener Koagulatorkonzentration wahrscheinlich eine verschieden grösse Anzahl von Primar teilchen enthalten."

We find that of the three sols this drop is observed for the two with a smaller initial charge. From the above discussion it will appear that these two sols will contain a greater ratio of primarily adsorbed chlorine ions to sulphide ions and the rearrangement of the molecules referred to above is more likely to affect the adsorptive power of the surface for the chloridions whose adsorption is weaker than that of the sulphide ions. The explanation given above has obviously its limitations but is put forward as a basis for further work.

The difference between the two type of sols regarding their capacity to adsorb chlorine ions may explain the varying stress laid by different authors on the effect of the anion on the coagulating capacity of cations so far as arsenions sulphide sols are concerned (Weiser, *J. Phys. Chem.*, 1921, **25**, 680 ; Dhar and Ghosh, *J. Phys. Chem.*, 1927, **31**, 187).

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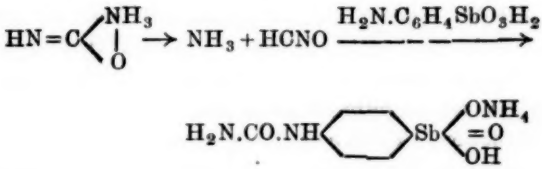
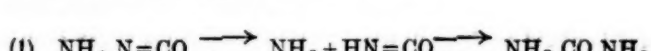
Organo-Antimony Compounds. Part III.

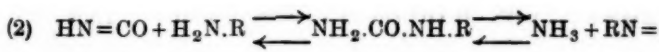
By Sudhir Chandra Niyogy.

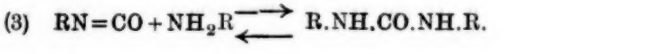
The constitution of Brahmachari's " Ureastibamine " has been the subject of controversy. Although Brahmachari in his first paper (*Ind. J. Med. Research*, 1922, **10**, 508) regarded the substance as a urea salt of 4-aminophenyl stibinic acid yet in a subsequent communication (*ibid*, 1924, **12**, 423) Brahmachari and Das considered it as the carbamino derivative of the ammonium salt of 4-aminophenyl stibinic acid. According to them the reaction proceeds as follows:—



Davies and Underwood (*J. Amer. Chem. Soc.*, 1922, **44**, 2595) had shown that the reaction between urea and an amine is a reversible one and proceeds as follows:—







In the process of Brahmachari (*loc. cit.*) a large excess of urea has to be used and the question has been raised why a compound of the type $CO(NH.C_6H_4SbO_3H{\cdot}NH_4)_2$ has not been isolated. Further the product is still held by some to be an eutectic mixture and not a true chemical compound.

The reaction between urea and the amine seems thus to depend mainly on the urea dearrangement (1). This reaction seems to take

place at 100° while the disubstituted ureas are formed, as shown by Davies and Underwood (*loc. cit.*) by the breaking up of the monourea derivative into the corresponding *i*socyanate, which takes place only above 168°. It is thus evident that on account of the lower temperature during the reaction the only product is the monourea derivative, or " Ureastibamine. "

The constitution of the ureastibamine has also been determined from another standpoint. It is well known that cyanic acid reacts with amine to form a urea derivative.

$$R.NH_2 + HN : CO = R.NH.CO.NH_2$$

If to an aqueous solution of the sodium salt of 4-aminophenyl stibinic acid an equivalent quantity of potassium cyanate is added and the solution is then acidified with dilute mineral acid, an almost colourless amorphous product immediately separates which is insoluble in excess of dilute mineral acid and does not give diazo reaction, but vigourous evolution of nitrogen takes place upon the addition of sodium nitrite solution. These behaviours show that the substance is not an amine but an amide, formed according to the following equation :—

$$H_2O_3Sb{\cdot}C_6H_4{\cdot}NH_2 + HN : CO = NH_2.CO.NH.\ C_6H_4.SbO_3H_2.$$

When this substance is dissolved in ammonia and a large excess of alcohol is added to the solution, a product separates which cannot be anything but the carbamino-derivative of the ammonium salt of 4-aminophenyl stibinic acid and is identical, both chemically and physiologically, with Brahmachari's ureastibamine. Thus it is definitely proved that ureastibamine is a chemical compound and not a mixture.

The method for the preparation of ureastibamine, as published by Brahmachari (*loc. cit.*) is lacking in experimental details and attempts to prepare it by the published method were not successful. When to a water suspension of 4-aminophenyl stibinic acid urea is added, the stibinic acid goes into solution but the product that is precipitated by the addition of alcohol is not the required compound but appears to be the urea salt of 4-aminophenyl stibinic acid. If on the other hand the condensation is carried out in slightly alkaline or acid medium, the product is merely the ammonium salt of 4-aminophenyl stibinic acid. To obtain the true ureastibamine,

the solution of the stibinic acid with urea had to be heated in a boiling water-bath for 3-4 hours.

A remarkable fact was noticed in the course of this work. Ureastibamine (which is the ammonium salt) is an extremely active agent for the destruction of the kalaazar parasites but the corresponding sodium and potassium salts, although less toxic and more stable, are without any marked action.

Experimental.

The preparation of 4-aminophenyl stibinic acid has been described previously (Niyogy, this *Journal*, 1928, **5**, 285).

Condensation of 4-Aminophenyl stibinic Acid and Urea.

(*a*) *In neutral solution.*—4-Aminophenyl stibinic acid (about 4 gms.) was suspended in water (50 c.c) and to this was gradually added solid urea (about 20 gms.) till the whole of the stibinic acid had gone into solution. It was sometimes necessary to warm the reaction mixture on a water-bath during the addition of urea. This solution was then filtered and treated with a large excess of alcohol. A gelatinious precipitate separated which was filtered off, washed with absolute alcohol till free from urea, and dried in a vacuum desiccator over fused calcium chloride; yield about 3 gms.

Properties.—It dissolved in water forming a red solution. On adding dilute acetic acid to the water solution the free acid separated which dissolved readily when a few drops of hydrochloric acid were added. It gave the diazo reaction. Apparently the substance had a free amino group and could not be ureastibamine. (Found: C, 25·78 ; Sb, 37·48. $NH_2.C_6H_4.SbO_3H_2.CO(NH_2)_2$, requires C, 26·09 ; Sb, 37·2 per cent).

(*b*) *In presence of acetic acid.*—The condensation was carried out as described before but a small quantity of acetic acid was added to the suspension of the stibinic acid, before the addition of urea, and the solution was heated on a water-bath for half an hour. The product now obtained had identical properties with the compound described before but the analytical data showed it to be the ammonium salt of 4-aminophenyl stibinic acid. (Found: C, 25·27; Sb, 42·7. $NH_2.C_6H_4.SbO_3H.NH_4$ requires C, 25·9; Sb, 43 per cent.)

Preparation of the Ammonium Salt of 4-Carbamidophenyl stibinic Acid.

4-Aminophenyl stibinic acid (about 4 gms.) in water suspension was treated with solid urea and the reaction vessel was heated in a boiling water-bath for 3-4 hours and left overnight. The solution was then filtered off from the separated solids and again allowed to stand overnight. This was again filtered from separated solids, if any, and treated with a large excess of alcohol, when an almost colourless amorphous substance separated. This precipitate was allowed to settle, filtered, and washed repeatedly with alcohol till free from urea and dried in a vacuum desiccator over fused calcium chloride. (Found: C, 25·45; Sb, 36·6. NH_2. CO. NH. C_6H_4 SbO_3H. NH_4 requires C, 26·09; Sb, 37·2 per cent).

Properties.—It dissolved easily in water forming a red solution. With dilute acetic acid the solution gave a precipitate which did not dissolve in excess of dilute hydrochloric acid. It did not give diazo reaction but nitrogen was given off when the acid solution was treated with sodium nitrite.

The analytical data as well as the chemical properties of the solution correspond with Brahmachari's ureastibamine.

Preparation of the above Compound from the Sodium Salt of 4-Aminophenyl stibinic Acid and Potassium Cyanate.

Sodium salt of 4-aminophenyl stibinic acid (6 gms.) was dissolved in water (50 c. c.) and potassium cyanate (3 gms.) was added to it. To the cold solution acetic acid (6 c. c.) was gradually added. A light brown percipitate separated, which was shaken for sometime and allowed to stand overnight. To the contents of the flask hydrochoric acid (10 c. c , *d*1·12) was added and thoroughly mixed. The precipitate was then filtered off, washed till free from acid, and suspended in water. The water suspension was divided into three parts. To the first portion dilute ammonium hydroxide was added drop by drop till the whole of the suspended solid had gone into solution. This was allowed to stand overnight, filtered off and treated with a large excess of alcohol. The precipitate that now separated was identical, both in chemical and physiological properties, with Brahmachari's ureastibamine. (Found: C, 25·82; Sb,

36·91. NH_2. CO. NH. $C_6H_4SbO_3H.NH_4$ requires C, 26·09; Sb, 37·2 per cent.)

The second portion was well cooled in ice, and cold dilute caustic soda was very slowly added till the whole of the solid had dissolved (avoid excess of alkali). The solution was then allowed to stand for some hours, filtered and treated with an excess of alcohol when the sodium salt separated. (Found: Na, 7·21; Sb, 36·2. NH_2. CO. NH. $C_6H_4SbO_3HNa$, requires Na, 7·03; Sb, 36·7 per cent.)

The third portion was similarly treated with caustic potash when the potassium salt was obtained. (Found: K, 11·56; Sb, 34·61. NH_2. CO. NH. $C_6H_4SbO_3HK$ requires K, 11·3; Sb, 34·98 per cent.)

I desire to convey my thanks to Prof. H. K. Sen for the interest he has taken in this work.

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Jute Seeds—*Corchorus Capsularis*. Part II.*

The Composition of Oil Corchorus.

By Nirmal Kumar Sen.

The object of this investigation was to determine the constituents of a specimen of jute-seed oil, in addition to making a study of the chemical composition of the seeds.

A large sample of jute seeds (*Corchorus capsularis*) was received from the Monipur Agricultural Farm, Dacca. They were dried, powdered and extracted with light petroleum ether in a large copper Soxhlet's apparatus and the oil obtained from the extract was used for the investigation, the results of which are given below.

Partial analysis of the crude oil was made by the author in a previous paper (this *Journal*, 1927, **4**, 205). It has been recently reported that the oil is now being largely used with highly satisfactory results by the natives of Hill Tippera, Bengal, as a specific for skin diseases (N. C. Chowdhury, "Jute in Bengal," p. 48). In Hill Tippera, the oil is extracted by the following crude process. "The seed is at first pounded and then moistened with water. This paste is put into a vessel with perforated bottom. Another vessel is placed beneath it to collect the oil dropped down. A third vessel or earthen pot with ignited charcoal within is kept over the first vessel, containing the paste. The heat is continued until the oil is fully extracted" (*cf.* Chowdhury, *loc. cit.*). The yield is reported to be one seer of the oil from 5 seers of the seed—*i.e.*, 20 per cent. of the seeds, but a sample of the seeds, used by the author, gave only 14·73 per cent. of the oil on extracting with light petroleum ether (b. p. 40°-60°).

Physical and Chemical Examination of the Oil.

The petroleum extract of the seeds was a yellowish brown oil. The last trace of petroleum ether was removed by heating in a vacuum. On standing the oil deposited a small amount of solid, forming a dry adherent film on glass at the ordinary temperature. The oil burnt with a bright, odourless, almost non-sooty flame on a wick of 4 mm. thickness and the length of the flame was 45 mm. There was no deposition of crust and the consumption was 6 grams per hour. The oil did not give any colour reaction with Baudouin

* Communicated, in abstract, to the Indian Science Congress, January, 1928.

and Halphen tests. Preliminary test showed the possible presence of archidic and lignoceric acids in the oil by the flocculent precipitate of the soap solution in 90 per cent. alcohol at the ordinary temperature (Holde, "Hydrocarbon Oils and Saponifiable Fats and Waxes," p. 388). The oil became rancid on standing in air.

Attempts to refine the oil by treatment with a solution of caustic soda was found useless on account of the difficulty met with in breaking the emulsion when once formed. For experimental purpose, the following method of refining was adopted, which gave satisfactory results:—A lot of 100 grams of the oil was well ground up in a dish with 50 grams of solid anhydrous sodium carbonate and 50 c.c. of water. The mass was then dried on the water-bath and the residue was again stirred up with coarsely powdered pumice stone, previously saturated with a 10 per cent. solution of caustic soda and ignited. The whole mass was then exhausted in a Soxhlet's apparatus with dry ether, the ether evaporated off and the oil heated in a current of carbon dioxide at 110°. 80·5 Grams of a light yellow oil with an acid value of 1·5 were obtained. Attempts to bleach the oil by Fuller's earth and bone charcoal were unsuccessful. The refined oil was used for determining its constants and composition. A few constants of the crude oil were determined by the author (*loc. cit.*) and the values are given in Table I together with those obtained for the refined oil.

TABLE I.

	Refined oil.	Crude oil.
Specific gravity at 28°	0·923	0·921
Refractive index	1·4615 at 29·7°	1·4705 at 30·1°
Solidifying point	—20°	—
Iodine value	102·6 (Hubl's)	109·2 (Wij's)
Saponification value	184·6	184·4
Acid value	1·5	24·07
Acetyl value	27·3	—
Reichert-Meissel value	0·16	—
Unsaponifiable matter % (Spitz and Hönig) ...	2·25	3·0
Soluble acids (% of butyric acid)	0·32	—
Insoluble acid % (Hafelmann and Steiner) ...	94·1	—
Glycerol %	9·2	—

The iodine value would indicate a semi-drying oil. The drying power of the oil was determined by spreading it over a glass plate 5 cm. by 10 cm. at ordinary temperature but only a trace of film was developed on the glass plate after a fortnight. The low Reichert-Meissel number showed that only a trace of glycerides of lower fatty acids was present while the high acetyl value indicated large amount of glycerides of the hydroxy acid.

Hydrolysis of the oil.

For a complete examination of the oil, 300 grams were employed. t was first subjected to distillation with steam but the distillate contained no volatile oil. The oil after separating from water, was hydrolysed by heating with alcoholic potash and benzol and the unsaponifiable matter was removed with naphtha by the gravimetric method of Spitz and Hönig. After evaporating off the alcohol from the soap solution, the residue was dissolved in a little water and decomposed with excess of dilute sulphuric acid in the presence of petroleum ether in a separating funnel. The acid layer was run off and the resulting fatty acid solution was washed with concentrated solution of Glauber's salt and twice with distilled water till the wash-water did not turn methyl orange red. The petroleum ether was dried for a short time with calcium chloride, filtered and distilled and the residual fatty acids were dried. A small quantity of insoluble oxy-acids separated between the acid and the petroleum ether solutions. This was filtered, well washed with petroleum ether, dissolved in warm alcohol, dried at 105° after evaporation of the alcohol and weighed. This amounted to 1·8 per cent. of the oil used.

The fatty acids.

The insoluble fatty acids were then separated into saturated and unsaturated acids by (*i*) the lead-salt-ether method and by (*ii*) Twitchell's lead-alcohol method (*J. Ind. Eng. Chem.*, 1921, **13**, 806).

Table II gives the percentage of the saturated and the unsaturated acids as estimated by the two methods.

TABLE II.

	Unsaturated acids.	Saturated acids.
Lead-salt-ether method	76·89%	23·1%
Lead-alcohol method	80·2	19·6

The saturated acids obtained by method (*ii*) were practically free from unsaturated acids as the iodine value determined by Hubl's method was found to be 2·1 and after crystallisation from alcohol; the iodine value was 1·3 as compared with a value of 19·03 for the saturated acids obtained by method (*i*).

Table III gives the analytical constants of the insoluble acids as well as the saturated and unsaturated acids. The molecular weight of the unsaturated acids was obtained by heating the acids with an excess of alkali and then titrating the excess. The usual method of direct titration gave result much higher (300·2).

TABLE III.

	Insoluble acids.	Saturated acids.	Unsaturated acids.
Melting point	31·5°-32·7°	50°-52°	—
Refractive index at 29·7°	1·4565	—	—
Titer (solidifying point).	29·9°	—	—6°
Iodine value (Hubl's)	114·51	2·1	141·45
Saponification value	200·2	216·7	196·4
Mean molecular weight	280·2	258·9	285·6

Unsaturated Acids.

In order to ascertain the nature of the constituents of the unsaturated acids a portion of the unsaturated acids (30 grams) was oxidised in alkaline solution with 1½ per cent. solution of potassium permanganate at the ordinary temperature with constant stirring. At the end of operation, sulphurous acid was added to the mixture until all the manganese oxide had dissolved. A pure white precipitate was then obtained which was separated by filtration and treated with naptha (b.p. under 50°) and the undissolved acids were digested with a large quantity of ether at the ordinary temperature. The ethereal solution, after the removal of the solvent, yielded the product which when crystallised from 96 per cent. alcohol separated in beautiful hexagonal plates melting at 135°. (0·2130 neutralised 6·7 c.c. of N/10 caustic potash. Neutralisation value=176·05. $C_{18}H_{36}O_4$ requires 177·6). This substance was evidently

dihydroxy-stearic acid and its formation proved the presence of oleic acid in the mixture of liquid acids. The portion of the oxidation product remaining undissolved by the above described treatment with ether was repeatedly boiled with large quantities of water and the liquid filtered. The filtrate yielded a crystalline deposit melting at 165° which, after crystallisation from alcohol, separated in small thin needles melting at the same temperature (0·1344 neutralised 3·85 c.c. of N/10 caustic potash. Neutralisation value 160·4 ; $C_{18}H_{36}O_6$ requires 161·2). This substance was thus identified to be tetrahydroxy-stearic acid (sativic acid) and its formation proved the presence of linolic acid in the oil. As no hexahydroxy-stearic acid could be isolated from the product of oxidation it may be concluded that linolenic acid is not a constituent of the oil.

As the foregoing method is not a quantitative one and is only useful to prove the presence of oleic acid in the unsaturated acids, the quantity of their constituents was determined by means of their bromine addition products as recommended by Jamieson and Baughmann (*J. Amer. Chem. Soc.*, 1920, **42**, 1198). Accordingly, the unsaturated acid prepared according to the method of Eibner and Muggenthalor (Lewkowitch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th edition, Vol. I, p. 585) were dissolved in dry ether and the mixture cooled to −10° ; bromine was added slowly drop by drop. During the addition of bromine, the temperature was not allowed to rise above −5° and the mixture was allowed to stand for two hours at about −10°. No precipitate insoluble in ether was obtained. The excess of bromine was then removed from the ethereal solution by washing in a separating funnel with an aqueous solution of sodium thiosulphate. The ethereal solution was then dried by anhydrous sodium sulphate and filtered. The ether was removed by distillation and the residue was dissolved in hot petroleum ether. After standing in an ice-chest overnight, the insoluble tetrabromide was filtered through a weighed Gooch crucible. The filtrate was concentrated to less than half of its original volume and again cooled and allowed to stand as before. After filtering this crop of tetrabromide crystals, the filtrate was evaporated to a volume of 35 c.c. and allowed to stand in the ice-chest overnight when no more crystals separated. Each crop of crystals was found to melt at 113°-114°, the melting point for tetrabromo-linolic acid. Finally all of the petroleum ether was removed and the residue weighed. The bromine content of the residue was then determined.

The data of the analysis of the bromo-derivatives are given below:—

	Gm.
Sample of unsaturated acids	3·5806
Linolic tetrabromide insoluble in petroleum ether, m.p. 113°-114°	2·7151
Residue (dibromide and tetrabromide)	3·8960
Bromine content of residue	41·954%
Dibromide in the residue 66·33% or	2·5842
Tetrabromide in residue 33·67% or	1·3118
Total tetrabromide found	4·0269
Linolic acid equivalent to tetrabromide 1·879 g. or	52·48%
Oleic acid equivalent to dibromide 1·6487 g. or	46·05%

That the tetrabromide was still present in the residue was proved by the fact that methyl alcohol extracted a further quantity of tetrabromide melting at 112°.

The percentage of linolic and oleic acids in the unsaturated acids were converted into the percentage of glycerides in the original oil as follows:—

	Found.	Calculated on basis of 100 %.	Original oil.	Glycerides in original oil.
Oleic acid	46·05%	46·76%	37·50%	39·18%
Linolic acid	52·48	53·24	42·70	44·63
Total	98·53	100·00	80·20	83·81

The theoretical iodine value of a mixture consisting of 46·76 per cent. oleic acid and 53·24 per cent. linolic acid is 138·67 which fairly agrees with the observed iodine value of the unsaturated acids (141·45).

Saturated Acids.

Attempted separation of higher saturated acids by recrystallisation from alcohol.—The solid fatty acids separated by Twitchell's method were fractionally crystallised from 90 per cent alcohol at 15° when the least soluble fraction on further crystallisation melted at 70°-71°. It was thus evident that some acid of higher carbon content than stearic acid was present and the substance on further crystallisation melted at 74°-75°. (0·2112 g. neutralised 5·7 c.c. of N/10

caustic potash. Neutralisation value=151·13). The product evidently consists of a mixture of archidic and lignoceric acids, the latter predominating. In order to ascertain the quantity of the "crude archidic acid," Renard test (*Compt. rend.*, 1871, **73**, 1330) for archidic acid was applied to the oil. Accordingly the fatty acids from 16·66 gms. of the oil were dissolved in 100 c.c. of 90 per cent. alcohol and precipitated by adding 1·6 grams of lead acetate in 50 c.c. of 90 per cent. alcohol. After standing overnight the separated lead salts were decomposed by 5 per cent. hydrochloric acid and the solid acids thus obtained were dissolved in 100 c. c. of 90 per cent. alcohol by warming and then cooled for thirty minutes in ice-water at 15°. The crystals were separated by suction and washed three times with 90 per cent. alcohol cooled at 15°. Finally the crystals were thoroughly washed with 70 per cent. alcohol until the washings remained clear on adding water. The filtrate and washings were measured. The crystals were then dissolved in absolute alcohol and weighed after drying at 100°. The correction for the amount in solution was then added to the amount found. The total yield was found to be 0·2825 gm. (corr.), which melted at 71°, (capillary tube method) and the percentage of the "crude archidic acid" was found to be 1·69 in the oil.

The fatty acids obtained after evaporating off the alcohol from the mother-liquor of the "crude archidic acid" were fractionally crystallised from 75 per cent. alcohol and the fractions representing the two extremes of solubility, which melted at 57°–59° and 53°–55·5° respectively, were analysed with the following results:

I. Fraction melting at 57°-59°.
0·2812 neutransed 10·16 c.c. of N/10 caustic potash.
Neutralisation value=202·3

II. Fraction melting at 53°-55·5°.
0·2006 neutralised 7·15 c.c. of N/10 caustic potash.
Neutralisation value=199·6.

These results showed that both of the above fractions consisted of a mixture of palmitic and stearic acids.

It was however found that the composition of the mixture was unchanged on re-crystallisation from alcohol and thus acted as a chemical entity. It was therefore not possible to separate such acids by fractional crystallisation and the compounds with their constant melting point and molecular weight would appear as chemical entities by the usual purity criteria.

In view of these facts it was thought advisable to separate the saturated fatty acid constituents of jute seed oil by the distillation of their methyl ester in vacuum and a sufficient quantity of the material is now being prepared for further analytical work which will form the subject of a subsequent communication.

Unsaponifiable Matter.

A portion of the unsaponifiable matter prepared by the method of Spitz and Hönig when dissolved in alcohol and the solution concentrated deposited beautiful crystals after standing overnight which after crystallisation from 90 per cent. alcohol was obtained in long thin lamina.

The melting point was not sharp, at 114° it softened and at 126° it was liquified and on twice crystallisation from alcohol it melted at 128°. It was optically active and was precipitated by digitonin and gave the characteristic Liebermann-Burchard colour reaction for a phytosterol. The air dried digitonide from the unsaponifiable matter was powdered and extracted with ether, then the digitonin separated by heating with acetic anhydride for 30 minutes. The separated acetates crystallised from alcohol and melted at 128° – 129·5°. Evidently it showed that it was not a single substance but formed mixed crystals of sterols.

The percentage of sterol was determined by the digitonide method of Windaus. The unsaponifiable matter from 20·21 gms. of the oil was warmed with 25 c.c. of 95 per cent alcohol and mixed with 25 c. c. of hot 1 per cent. solution of digitonin in 96 per cent. alcohol. After standing overnight the precipitate was filtered on a weighed Gooch crucible, washed successively with alcohol and ether, dried at 110° and weighed. The sterol amounted to 0·6145 per cent. in the oil. The unsaponifiable matter had an iodine value of 62·15 and the alcoholic mother-liquor left after the separation of sterol by crystallisation yielded on evaporation a small quantity of yellow resinous substance having a characteristic smell. When boiled with acetic anhydride it dissolved completely and on cooling the lower layer of the solution was clear but a magma of crystals separated out on the top of the liquid thus indicating the propable presence of some higher alcohol of aliphatic series. On account of the very small amount of the material it could not be further examined.

Summary.

The chemical and physical characteristics of a sample of extracted jute seed oil have been determined. A study has been made of the composition of the oil, the results of which are given below:—

Glycerides of oleic acid	...	39·18 per cent.
,, ,, linolic acid	...	44·63

The oil contains a small quantity of "crude archidic acid" (0·169 per cent.) and palmitic and stearic acids. From the unsaponifiable portion of the oil a very small amount of a phytosterol was obtained. When purified, the oil is suitable as a food and is also satisfactory for burning purpose.

My sincere thanks are due to Prof. J. C. Ghosh and Prof. S. N. Bose for their kind interest and encouragement during the progress of the work.

CHEMICAL LABORATORY,
DACCA UNIVERSITY.

Received September 13, 1928.

On an Inductive Method for the Study of Natural Products. Part I. The Naturally Occurring Anthraquinone Derivatives.

By P. C. Mitter and Harogopal Biswas.

Although a large number of anthraquinone derivatives present in nature have been known for a long time, it is only during recent years that the constitutions of some of the most important members of this group have been determined with certainty. We would refer to the synthesis of chrysophanic acid by Eder and Widmer (*Helv. Chim. Acta*, 1922, **5**, 3) and of emodin by the same authors (*Helv. Chim. Acta*, 1923, **6**, 966) and also by Jacobson and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 1312), of morindone by Jacobson and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 2788) and of rubiadin by Mitter and Gupta (this *Journal*, 1928, **5**, 25).

An examination of these and other naturally occurring anthraquinone derivatives reveals the fact that only certain definite configuration of methyl and hydroxyl groups are present in them and also that it is possible to classify them under four distinct heads.

The following empirical laws are found to hold good in the case of anthraquinone derivatives present in plants.

(1) No naturally occurring anthraquinone derivative contains more than four substituent groups in the two benzene nuclei, namely, not more than *one* methyl (or carboxyl or carbinol group) which, if present, always occupies a β position, and not more than *three* hydroxyl groups.

(2) The substances containing the maximum number of substituents form the fundamental types and the other anthraquinone derivatives occurring in the same plant are all derived from this fundamental type being either oxidation or reduction or etherification etc., products of the same. The fundamental types are therefore also derivable by superposing the formulae of associated anthraquinones.

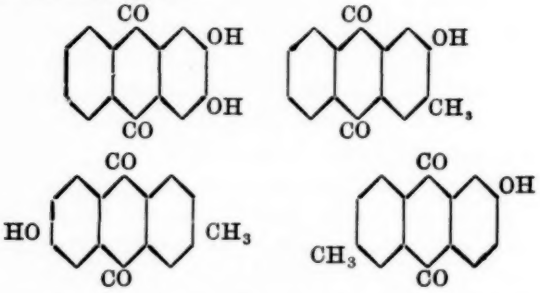
(3) Of the four substituents two (including the methyl or carboxyl or carbinol group, if present) occupy β-positions and the other two occupy α-positions.

(4) If both the β-substituents are in one ring the other groups also occur in the same ring or in other words, a homonuclear type is formed. If both the β-substituents are OH groups they must occur in the same ring.

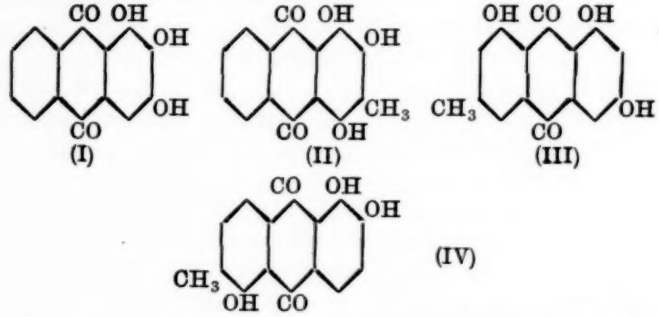
(5) If the β-substituents are in different rings the α-substituents are distributed in such a way as to produce a symmetrical configuration.

As no two types have three groups in common, it is possible by examining any one naturally occurring anthraquinone containing three substituents (sometimes even two substituents) to determine the fundamental type from which this particular substance and *all the other anthraquinone derivatives associated with it* have been derived.

Starting from anthraquinone we get by substituting two β-positions by two hydroxyl groups or by one hydroxyl and one methyl group the following types:—



From these four β-substituted products we can derive the four fundamental types of naturally occurring anthraquinones—two homonuclear and two heteronuclear.



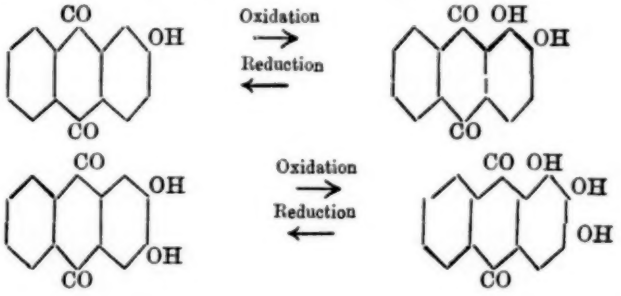
These exhaust, barring a few apparent exceptions which we hope to be able to show also conform to the above four categories—the anthraquinone derivatives occurring among plant products.

As regards the relative position of the hydroxyl groups it is interesting to note that the alizarin grouping (1:2) can occur in three out of the four fundamental types:—Chayroot, madder and morindone.

It is also interesting to note that while the 1:6-grouping is common both to the morindone and the emodin types, the anthrarufin (1:5)-grouping is present only in the morindone type while the chrysazin grouping (1:8) is present only in the emodin type. The diagnostic value of these observations will be apparent later on.

Type I (*Chayroot type*).

Our knowledge about this group is derived from the works of A. G. Perkin and Hummel (*J. Chem. Soc.*, 1893, **63**, 1160; 1895 **67**, 817). The substances isolated from chayroot are 2-oxyanthraquinone, alizarin, alizarin-*O*-methyl ether, anthragallol-1:2-dimethyl ether, anthragallol-1:3-dimethyl ether and hystazarin monomethyl ether. They may be all regarded as derived from anthragallol by permutation and combination of the hydroxyl groups, at least one β standing hydroxyl group, being present. Another way of looking at the products would be to consider them as members of oxidation and reduction chains as follows:—

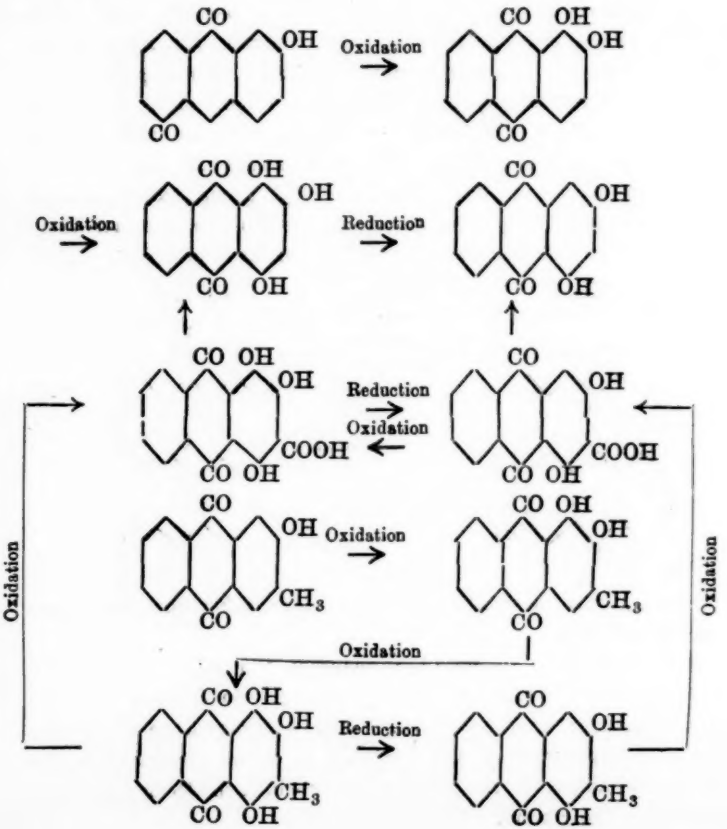


So far, only derivatives of these four substances have been found in chayroot.

It is interesting to note that chayroot, the root of *Oldenlandia umbellata* (Linn) *Rubiaceæ*, although belonging to the same natural order as madder does not contain any anthraquinone derivative with a methyl group in the nucleus. It is an illustration of the non-superposability of the types, without which the theory would at once fall to the ground.

Type II (*Madder type*).

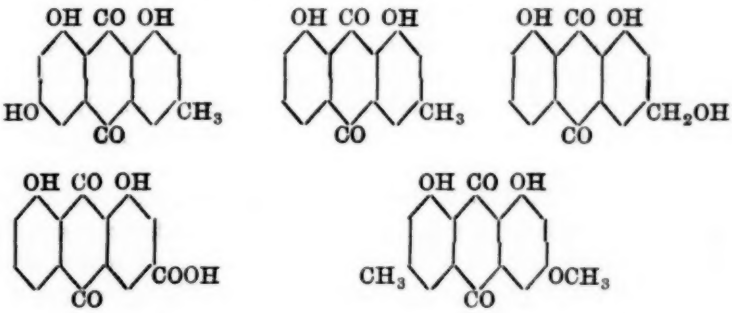
The anthraquinone derivatives of the madder type have been very largely investigated and a complete bibliography up to 1918 will be found in "The Natural Organic Colouring Matters" by Perkin and Everest (pp. 35). All the members of this type (with the exception of Munjisthin which we are now investigating) may be derived from 3-methylpurpurin, a substance which is probably present in madder but which we have been unable, up to the present moment in isolating from it, although attempts are being made in that direction. They can also be regarded as members of oxidation and reduction chains.



As already indicated, the real value of this hypothesis would depend on the non-existence of mixed types. There are on record two cases which are apparent exceptions to this rule. Hugo Muller (*J. Chem. Soc.*, 1911, **99**, 968) had found traces of alizarin in rhubarb. As he had investigated residues which had accumulated in course of a long series of investigations extending over many years and only obtained minute traces of alizarin, the chances of possible contamination of the starting materials with alizarin containing materials cannot be altogether ignored. In the second place we have Simonsen's observation about the presence of rubiadin monomethyl ether in *Morinda citrifolia* (*J. Chem. Soc.*, 1920, **117**, 561) along with morindone (*J. Chem. Soc.*, 1918, **113**, 766).

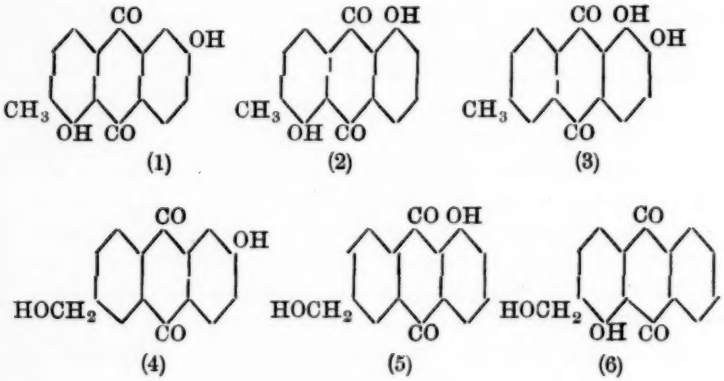
As against this we have the observation of Barrowcliff and Tutin (*J. Chem. Soc.*, 1907, **91**, 1909) who had found, in the root of *Morinda longiflora*, alizarin monomethyl ether and rubiadin monomethyl ether but no morindone. Whether the case observed by Simonsen is really an exception to the general rule formulated before or whether as Simonsen observes that "it is possible that the latter (*Morinda longiflora*) might at some period of its growth contain morindin, since the quantity of glucoside appears to vary with the age of the bark (*loc. cit.*), is difficult to say at the present moment.

(3) In the emodin group, the following substances are known:—



It will be observed that they are all derivable from one fundamental type. We are now engaged in the synthesis of other anthraquinone derivatives of the same type containing the same or a smaller number of groups with a view to identifying some of the lesser known products accompanying emodin.

(4) In the morindone group, the only substance of which the constitution is definitely known is morindone itself. From the foregoing it would be reasonable to expect that the products accompanying morindone would be related to it in the same way as the anthraquinones of the other three types to the fundamental types. Thus, a substance whose analytical data and properties agree with that of a dihydroxy-derivative of a methyl anthraquinone would be one of the following:—



The first of these compounds has been synthesised by Simonsen and Rau (*J. Chem. Soc.*, 1921, **119**, 1340). It melts at 281° and its acetyl derivative melts at 212°.

In their investigation of Mang-Koudu, the root bark of *Morinda umbellata*, Perkin and Hummel (*J. Chem. Soc.*, 1894, **65**, 851), describe the presence of a substance of m. p. 281° the analysis of which agrees more or less with that of dihydroxymethylanthraquinone. (C, 69·31; H, 4·09 instead of C, 70·86; H, 3·93 per cent.).

Oesterle and Tisza (*Arch. Pharm.*, 1908, **246**, 150), have isolated from the root bark of *Morinda citrifolia* small quantity of a substance to which they gave the name Soranji-diol. It melted at 277°. The analysis of the acetyl derivative (m. p. 230°) agrees with that of di-acetoxy-methylanthraquinone although that of the hydrolysis product is somewhat divergent (C, 72·17; H, 4·04 instead of C, 70·86; H, 3·93 per cent.).

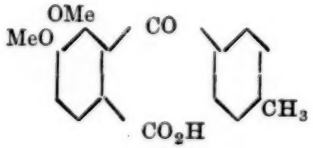
From the above we may reasonably conclude that the compound isolated by Perkin and Hummel and the Soranjidiol of Oesterle and Tisza was 2:5-dihydroxy-6-methylanthraquinone.

Oesterle and Tisza (*loc. cit.*) have found in *Morinda citrifolia* another dihydroxy-methylanthraquinone which they named Morindadiol dissolving in alkalis with an orange-red colour and in sulphuric acid with a cherry-red colour. It melted at 244° and the acetyl derivative melted at 229°.

The product (2), 1:5-dihydroxy-6-methylanthraquinone which we have synthesised, gives identical colour reaction and its acetyl derivative melts at 230°. But the hydrolysis product melts at 190°.

We have also synthesised (3) by condensing hemipinic anhydride with toluene in presence of aluminium chloride and treating the toluoylbenzoic acid so formed with sulphuric acid. We found that in the formation of toluoyl benzoic acid a methyl group is split off, thereby confirming Lagodzinski's supposition that in the condensation of hemipinic anhydride with benzene a hydroxy methoxy benzoyl benzoic acid is formed (*Ber.*, 1895, **28**, 1427) although it has been sometimes held that the splitting up of the methoxyl group takes place at the time of ring closing with sulphuric acid (Bentley and Weizmann, (*J. Chem. Soc.*, 1908, **93**, 435).

We have also assumed that in this condensation it is the CO-group next to the methoxyl groups which reacts and that the ketone group enters in *p*-position to the methyl group so that the resulting compound has formula (1) and not formula (2).



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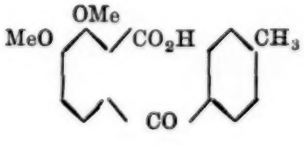

II

This has been demonstrated by Bistrzycki and Yssel de Schepper in the case of condensation of hemipinic anhydride with anisol (*Ber.*, 1898, **31**, 2800 ; *vide* also Simonsen and Rau, *J. Chem, Soc.*, 1921, **119**, 1339 (foot-note)). The formation of a compound of formula (1) in the first instance would explain the subsequent splitting off of the methyl group as it is well known that the presence of CO groups in *ortho*-position renders the methoxyl groups unstable. The anthraquinone melts at 220° and its acetyl derivative melts at 190°. But it does not agree with any natural product isolated so far.

Experimental.

1:5-*Dimethoxy*-6-*methyl-anthraquinone.*

1:5-Dinitro-6-methylanthraquinone was prepared according to the method of Eder, Widmer and Bütler by nitrating β-methyl-anthraquinone with nitric acid (*Helv. Chim. Acta*, 1934, **7**, 341). After separation from 1:8-dinitro-compound and recrystallisation from pyridine it melted at 335°. The 1:5-dinitro compound was then converted into 1:5-dimethoxy-6-methyl anthraquinone by the method of Kaufler (*Ber.*, 1904, **37**, 65). The dimethoxy compound crystallised from glacial acetic acid melted at 176°-177°.

(Found: C, 72·19 ; H, 4·91 ; OMe, 21·6. $C_{17}H_{14}O_4$ requires C, 72·34 ; H, 4·96; 2 OMe, 21·9 per cent.)

Demethylation of 1:5-*Dimethoxy*-6-*methyl-anthraquinone.*

The dimethoxy compound (0·5 g.) was dissolved in some 25 c.c. glacial acetic acid saturated with HCl acid gas and heated in a sealed tube for 2 hours at 190°-200°. After cooling the contents were transferred to a beaker by washing with water, boiled and after filtration the yellow mass dissolved in very dilute alkali to a red solution which on acidification gave a yellow precipitate. Recrystallised from glacial acetic acid it melted at 190°. (Found: C, 70·57 ; H, 4·07. $C_{15}H_{10}O_4$ requires C, 70·86 ; H, 3·93 per cent.)

Acetyl derivative of 1:5-*Dihydroxy*-6-*methyl-anthraquinone.*

It was prepared in the usual way and crystallised from alcohol ; m.p. 230°. (Found: C, 67·16; H, 4·21. $C_{19}H_{14}O_6$ requires C, 67·45; H, 4·14 per cent.)

On deacetylation a product was obtained which on crystallisation from glacial acetic acid was found to melt at 190°.

3-*Hydroxy*-4-*methoxy*-2-p-*toluoyl-benzoic acid.*

Hemipinic anhydride (10 g.) was suspended in 200 c.c. toluene and to this anhydrous $AlCl_3$ (20 g.) was added in small portions

and then the flask containing the mass was heated on a water-bath at 45-55° for 5 hours. The flask was then cooled in ice while dilute HCl (200 c.c.) was added and the toluene left in excess was removed by means of steam. The crude benzoylbenzoic acid obtained was boiled with $CaCO_3$, filtered and on acidifying the filtrate, white crystals of the benzoylbenzoic acid appeared (yield, 7 gms). Recrystallised from glacial acetic acid, 5 gm. of the acid m.p. 175-76° were obtained. (Found: C, 67·54; H, 4·83. $C_{16}H_{14}O_5$ requires C, 67·13; H, 4·89 per cent. Found: OMe, 10·13. $C_{15}H_{11}O_4(OCH_3)$ requires OMe, 10·83 per cent.).

Preparation of 1-Hydroxy-2-methoxy-6-methylanthraquinone.

To the benzoylbenzoic acid (5 g.) was added boric acid (5 g.) and sulphuric acid (10 g., sp. gr. 1·84). To the mixture were then added 50 gm. of fuming sulphuric acid (20% SO_3) and heated on the water-bath for 3 hours. It was then poured into ice when a brown mass was obtained. This was then boiled with a dilute solution of sodium carbonate and filtered. From the filtrate on acidification a gram of benzoylbenzoic acid was recovered. The crude anthraquinone weighed about 4 gm. On crystallisation from glacial acetic acid 3 gm. of orange yellow crystals of the anthraquinone, m.p. 200°, were obtained. (Found: C, 72·06; H, 4·53. $C_{16}H_{12}O_4$ requires C, 71·64; H, 4·48; per cent.).

Acetyl derivative—From the 1-hydroxy-2-methoxy-6-methylanthraquinone the acetyl derivative was prepared in the usual way. Crystallised from absolute alcohol it melted at 170°. (Found: C, 69·65; H, 4·45. $C_{18}H_{14}O_5$ requires C, 69·68; H, 4·52 per cent.)

Demethylation of 1-Hydroxy-2-methoxy 6-methyl anthraquinone. Preparation of 6-Methylalizarin.

One gram of the anthraquinone was mixed with 2 gm. of finely powdered $AlCl_3$ and heated to 220° in course of one hour and then kept at this temperature for half an hour. When cooled, the reaction mixture was carefully transferred to a beaker with water and then it was boiled with a few c.c. of concentrated hydrochloric acid till brown flakes appeared. It was filtered, dissolved in one per cent potassium hydroxide solution, filtered and the filtrate acidified when

thick yellow flakes appeared. Crystallised from glacial acetic acid the 6-methylalizarin obtained melted at 220°. (Found: C, 70·46 ; H, 4·20. $C_{15}H_{10}O_4$ requires C, 70·86 ; H, 3·93 per cent.)

Acetyl derivative.

It was prepared in the usual way. Crystallised from alcohol it melted at 190°. (Found: C, 67·22; H, 4·35. $C_{19}H_{14}O_6$ requires C, 67·45 ; H, 4·14 per cent.).

On deacetylation and sublimation of the product the m.p. was found to be 220°.

Further experiments are in progress.

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